

Experimental Chemistry
for
COLLEGES

BY

J. ALLEN HARRIS, PH.D.

*Associate Professor of Chemistry, The University of
British Columbia*

AND

WILLIAM URE, PH.D.

*Associate Professor of Chemistry, The University of
British Columbia*

DEPARTMENT OF EDUCATION
VICTORIA, B.C.

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EXPERIMENTAL CHEMISTRY

FOR

COLLEGES

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REVISED EDITION

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PREFACE TO THE SECOND EDITION

In this edition there are included five assignments dealing with qualitative analysis. These are intended to give the student an introduction to this field without presenting the complete scheme of analysis, and hence only two groups of cations are dealt with intensively, Groups I and III. The omission of Group II is made because of the experimental difficulty of the separations. Emphasis is laid on the necessity of separating the ionic constituents before specific tests can be applied and hence the work begins with the identification of the various groups of cations. It is believed that the manual will be found useful in many laboratories for more intensive courses in qualitative analysis.

EXPERIMENTAL CHEMISTRY

FOR

COLLEGES

In a number of the experiments, changes have been made where these have been found to produce more satisfactory results. The experiments are arranged in a series of assignments, each dealing with a particular group of cations. The experiments are arranged in a series of assignments, each dealing with a particular group of cations. The experiments are arranged in a series of assignments, each dealing with a particular group of cations.

—J. J. BOCHER, A. D. 1909
LEBANON, NEW HAMPSHIRE
1909, July

WILLIAM W. W.

PREFACE TO THE FIRST EDITION

This manual had its origin in a series of experiments drawn up for first-year students at the University of British Columbia and based on observations made by the authors during several years of laboratory direction at this and other institutions.

The experiments have been used and modified over a period of three years to suit the requirements of unskilled students and, in their present form, have been found to yield highly satisfactory results.

The necessity of getting away from the methods of laboratory instruction in elementary chemistry in which the student is asked to perform a large number of short and chiefly qualitative experiments, ending in the sink, is becoming apparent to most laboratory instructors. Such experiments are better suited to the lecture table, and it has been our experience that the interest of the student can best be aroused and maintained by giving him a definite objective to attain during each laboratory period, whether it be the quantitative testing of some chemical principle or the careful preparation of some interesting compound. The experiments have also been carefully chosen so that during their execution the student acquires a considerable knowledge of the chemistry of the process along with valuable experience in technique (such as fractional crystallization and distillation), without the need of separate experiments purporting to illustrate these operations but giving no indication of their importance or value in general chemistry.

The quantitative side of experimental work is emphasized, and even the preparation experiments are carried out with roughly weighed quantities of materials. This impresses upon the student the fact that reactions take place between definite quantities of materials and at the same time reduces waste to a considerable extent.

The course is arranged to accompany no particular textbook, as the individual assignments are made practically independent. In addition, each experiment is preceded by an introductory

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EXPERIMENTAL CHEMISTRY

"The chymists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly, that may I die if I would change places with the Persian King."

—J. J. BECHER, A. D. 1669.

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In this edition there are included five assignments dealing with qualitative analysis. These are intended to give the student an introduction to this field without presenting the complete scheme of analysis, and hence only two groups of cations are dealt with intensively, Groups I and III. The omission of Group II is made because of the experimental difficulty of the separations. Emphasis is laid on the necessity of separating the ionic constituents before specific tests can be applied and hence the work begins with the identification of the various groups of cations. It is believed that the experimental work in these assignments should serve to present many illustrations of the application of ionic theory and at the same time prepare the student for more intensive courses in qualitative analysis to follow.

In a number of the experiments, changes of procedure have been made where these have been found to produce more satisfactory results. In Assignment 6 the freezing point of salt solutions is considered from the point of view of complete ionization, and the calculation of apparent degree of ionization is omitted. The sections dealing with acids have been changed to introduce the hydronium ion, a step which is in line with modern teaching practice.

J. ALLEN HARRIS,
WILLIAM URE.

VANCOUVER, CANADA,
July, 1940.

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The course is arranged to accompany no particular textbook, as the individual assignments are made practically independent. In addition, each experiment is preceded by an introductory

section which discusses the field illustrated by the experiment, together with the theoretical considerations involved. This information has been found to be of value where there are large classes and individual instruction is not possible but does not detract from its value for those colleges where the quiz instructors have but few students in their sections. For the benefit of large classes the procedures are given in considerable detail.

Since the experiments are designed to give the student some experience in connection with a wide variety of laboratory processes, and consequently with a considerable number of important pieces of apparatus, it might appear that such a course would be too expensive for many elementary laboratories. We have found it quite feasible to subdivide a laboratory section of eighty students into four groups, each group working on an entirely different experiment. In this way the actual amount of apparatus necessary is only one-fourth and the apparatus may be used successively by each group. In the case of those preparations which require the use of a furnace, five small dental furnaces have been found sufficient to supply the needs of a whole laboratory section of the size mentioned above, operating in four groups.

Any difficulty in correlating the laboratory course with the lectures is more than offset by the fact that there is no waste of time in waiting for accurate balances as but one of the four groups need be assigned an experiment involving their use. The student is also expected to read other available literature concerning the experiment, so that in our experience we have found that he becomes better informed about the subject than when merely following the lecture course. For colleges adequately equipped with apparatus and instructors it is of course possible to have the laboratory experiments supplementary to the discussion of the lecture room.

At the end of the manual have been included a number of representative problems of a sufficiently advanced nature to satisfy the most ardent elementary student.

We wish to express our thanks to Prof. A. A. Noyes for permission to include his experiment on the silver ammonia complexion; to Prof. B. S. Hopkins for his encouragement in preparing the series of experiments for publication; and to Dr. H. L. Streight, Dr. F. L. Munro, Mr. D. W. Oswald, Mr. J. T. Young, and Mr. R. M. Archibald for their careful supervision, which has made possible the thorough testing of each experiment. To Prof. R. H. Clark, Head of the Department of Chemistry of the University of British Columbia, the authors are pleased to acknowledge their indebtedness for the opportunities which have made this work possible.

J. ALLEN HARRIS,
WILLIAM URE.

VANCOUVER, CANADA

August, 1932.

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INSTRUCTIONS TO STUDENTS

Note.—These suggestions for laboratory procedure follow certain features in the design of the manual or have been found to be effective in maintaining efficiency. The instructor may, of course, make modifications as he desires.

Before Coming to the Laboratory.—1. Read over the day's assignment carefully and be sure that you understand what you are expected to do. No excuses will be accepted for delay in commencing your work in the laboratory.

2. Refer to your textbook and to other reference books for additional information as to the theory of the experiment.

3. Remove from the manual the pages dealing with the assignment for that day and bring them to the laboratory in a loose-leaf folder.

Laboratory Reports.—1. Record all data as you read them. A copy of these must be left with the instructor before you leave the laboratory.

2. Your report on the assignment is to be submitted to the instructor *at the beginning* of the next laboratory period. This report should consist of:

a. All data obtained.

b. Calculations from data.

c. Answers to the exercises at the end of each experiment.

3. These reports will be graded and returned to you at the following laboratory period. Remember that the marks given will constitute a part of your final grade for laboratory work.

4. *At the end of the course, all of your assignments and reports must be filed in order in a laboratory book, fastened there, and turned in to the instructor for final grading. The complete manual constitutes the laboratory notebook.*

General Laboratory Procedure.—1. In beginning the course, wash all the glassware in your locker, using the cleaning solution provided, and rinse the reagent bottles on your desk with water, if they are dusty or dirty.

2. Refill any empty reagent bottles from the large reagent bottles provided.

3. Note the position of the reagents, both solid and liquid, and remember that only those on your desk are to be used there. The side-shelf reagents must never be taken away. When it is necessary to use these, take a clean test tube, graduate, or watch glass to obtain the reagent.

4. In the case of solids, remove these with a clean spatula, and be sure to replace the stopper when you have finished. The majority of these reagents are spoiled by exposure to air.

5. In the Preparation Experiments, your product must be shown to the instructor for his approval and then placed in the containers provided.

6. Any special apparatus which is set out for the experiment must be thoroughly cleaned after use and left in place.

7. Before leaving the laboratory each day, wash down the top of the desk, rinse off the reagent bottles, and be sure you have replaced all of your apparatus.

EXPERIMENTAL CHEMISTRY FOR COLLEGES

INTRODUCTION

Most failures in experimental work, as well as a great many accidents, are due to carelessly constructed or otherwise faulty apparatus. In the majority of cases, this condition is caused by failure of the student to follow directions closely. When a definite concentration or weight is given, it is imperative that such be used. The idea commonly met with on the part of the student that, if a little works well, a lot will work better is entirely erroneous—usually the converse is true.

All warnings and suggestions are given for the student's protection from possible injury and are well worth observing closely.

Do not be disappointed if first attempts at glass bending, etc., are not enormous successes; practice is necessary. The student is also reminded that the elementary laboratory course is not designed to turn out qualified chemists in one year, nor is it intended to serve as a source of amusement. The experiments have been carefully chosen for the purpose of permitting any student of average intelligence, and willing to work carefully, to prove to his satisfaction the validity of general laws and principles that govern the universe and upon which many important industries depend.

Above All—Be Honest.—Cheating in the laboratory is like cheating at golf, only one's self is deluded and reality will have to be faced eventually. It is better to obtain an honest yet poor answer than a good one that is not one's own. It is also well to remember that laboratory grades are based not solely on mathematical accuracy but also on technique and the student's attitude to his work in general.

By working carefully, excellent results from these experiments are possible, and the information obtained during the laboratory should help materially in clarifying the lecture course.

GENERAL LABORATORY PROCEDURE

During the course there may be a few terms used which the student will have to add to his chemical vocabulary. Some of the more important ones are given below.

Filtration.—When it is necessary to separate solid matter from a liquid by means of pouring the mixture through a filter paper, the process is known as filtration. The residue retained by the filter is known as the "precipitate" or "residue," while the filtered liquid is spoken of as the "filtrate" (Fig. 1).

Usually, gravity alone is sufficient to bring about separation, but in the cases of certain precipitates filtration is slow. In these instances, suction is used to hasten the separation. In Figs. 2a and 2b we have represented two types of filters known as "suction filters," in which ordinary

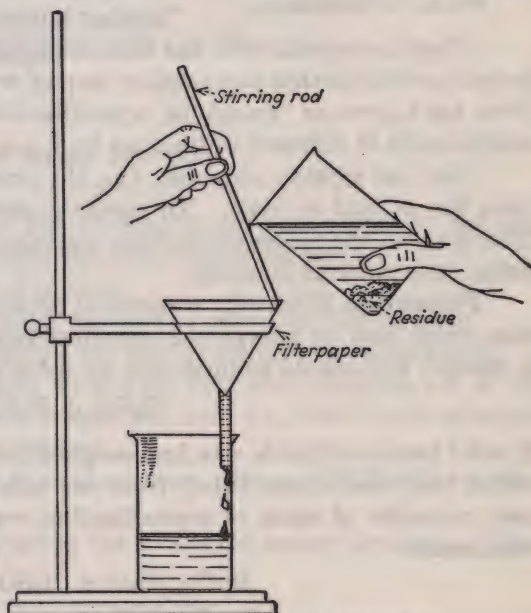


FIG. 1.—Filtration and decantation.

filter paper is used. If, however, the liquid is corrosive, such as hot acid or alkali solutions, filter paper is of no avail since it breaks easily. In such cases the filter paper cone is replaced by an "asbestos filter." This is represented in Fig. 3 and is prepared by first plugging the lower portion of the filter funnel with glass wool and then pouring over it (with the suction applied) a fine suspension of asbestos wool in hot water. Small porcelain filters of the Buechner type may be conveniently used where suction filtration is necessary.

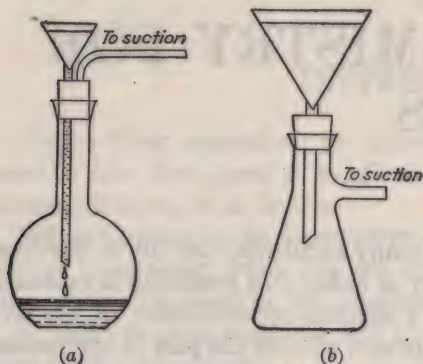


FIG. 2.—Suction flasks.

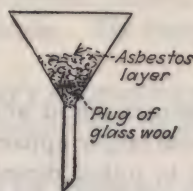


FIG. 3.—Asbestos filter.

Crystallization—Recrystallization.—In a great many preparations, a precipitate is not formed during the reaction. In order to obtain the product, the solution is evaporated gently so as to bring about a saturated condition. Since the solubilities of most salts are much greater at higher temperatures, if saturation is reached at these temperatures, on cooling the solution we bring about a "supersaturated" condition. Normally, the "excess" salt crystallizes out during the process of cooling, but in some cases a "supersaturated solution" results. When such occurs, crystallization may be brought about by simply scraping the inside wall of the container, beneath the solution, with a stirring rod, or a crystal of the same salt may be added. This latter process is known as "seeding," and the crystal that is added we speak of as a "seed crystal." The "crop" of crystals obtained from a solution is the "crystal meal," and the saturated solution from which it is obtained is termed the "mother liquor" (Fig. 4).

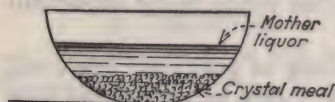
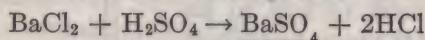


FIG. 4.—Crystallization.

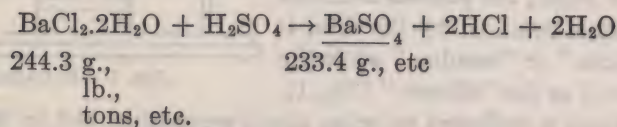
When the crystal meal has been removed by decantation or filtration, the mother liquor may be evaporated further and another crop of crystals obtained. Successive crystallizations such as these are known as "fractional crystallizations." This process is used extensively in separating soluble salts of different solubilities from one another.

The first crystals obtained, *i.e.*, the crystal meal, are usually relatively impure and smaller than the normal crystals. To separate any soluble impurities, "recrystallization" is effected. This involves the redissolving of the crystals in as small a portion of solvent as possible and crystallizing once more as formerly.

Percentage Yield.—In a chemical process we can express the reaction by means of an equation which may be interpreted quantitatively. For example, when a solution of barium chloride is treated with dilute sulfuric acid we write as the equation



If solid barium chloride was first weighed out, and reacted upon, we may write the proportions in which they react immediately from our balanced equation. Since solid barium chloride contains two molecules of water of crystallization, we must include them in the molecular weight of that compound:



Consequently if 244.3 g. of crystallized $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved and reacted upon by dilute sulfuric acid, the "theoretical yield" would be 233.4 g. of BaSO_4 . If, however, on weighing

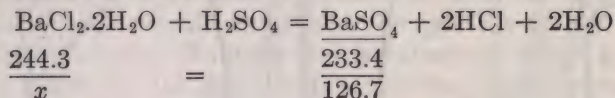
the BaSO_4 obtained it was found that only 200 g. of the sulfate were obtained ("actual yield") we speak of the "percentage yield" as being the value obtained by dividing the actual by the theoretical yield and multiplying by 100; *viz.*,

$$\text{Percentage yield of BaSO}_4 = \frac{200.00}{233.40} \times 100$$

Percentage Purity.—It is often necessary to determine the purity of a chemical compound. In such a case it is customary to bring about a reaction that we know will give us a "quantitative" or "theoretical" yield. By weighing the product and comparing this weight with those obtained from a study of the equation, we can calculate the actual weight of the pure substance in our original sample.

Taking the above reaction as an example—since when properly carried out the precipitation of barium as the sulfate is quantitative—suppose that a precipitate of BaSO_4 weighing 233.4 g. is obtained. Our equation tells us immediately that we must have had 244.3 g. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in our original sample. If the weight of the sample taken was such, we realize that the sample was pure barium chloride.

If, on the other hand, we weighed out 244.3 g. of impure barium chloride, and knowing that the conditions of precipitation were correct for obtaining a quantitative reaction, obtained a precipitate of BaSO_4 of only 126.70 g. weight, we realize at once that our original sample could not have been pure. The actual amount of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ present in the original sample can be readily calculated from the equation as follows:



or

$$x = 122.15 \text{ g.} = \text{actual weight of BaCl}_2 \cdot 2\text{H}_2\text{O in sample}$$

The percentage purity of the salt is then

$$\frac{\text{Actual weight of BaCl}_2 \cdot 2\text{H}_2\text{O in sample}}{\text{Total weight of sample}} \times 100$$

or

$$\frac{122.15}{244.30} \times 100 \text{ per cent} = 50 \text{ per cent pure}$$

Concentration.—By "concentration" we mean the amount of substance present per unit volume. Three common methods of expressing concentrations of solutions are:

1. The number of grams of solute per 100 ml. of solvent.
2. The number of gram-molecular weights of solute per liter of solution—the *molality*.
3. The number of gram-equivalent weights of solute per liter of solution—the *normality*.

A molal solution is one containing one gram-molecular weight per liter and is written 1*M* or 1*m*. A normal solution (1*N*) contains one gram-equivalent weight per liter, *i.e.*, that weight of solute which is equivalent to one gram-atomic weight of hydrogen.

Thus 6*N* HCl contains 6×36.5 g. of HCl per liter of solution, whereas 6*N* H_2SO_4 contains $6 \times 98\frac{1}{2}$ g. and is therefore 3*M*.

It is customary to express concentration by enclosing the formula in square brackets. Thus $[\text{HNO}_3]$ means "the concentration of nitric acid."

Weighing.—Two kinds of apparatus are to be used for weighing:

1. *Rough Balances or Platform Scales.*—These are to be used for objects weighing more than 100 g. and for determining approximate weights such as are required in the preparation experiments (Section B). These balances will weigh to about 0.1 g. The triple-beam type is convenient as it does away with the necessity for separate weights.

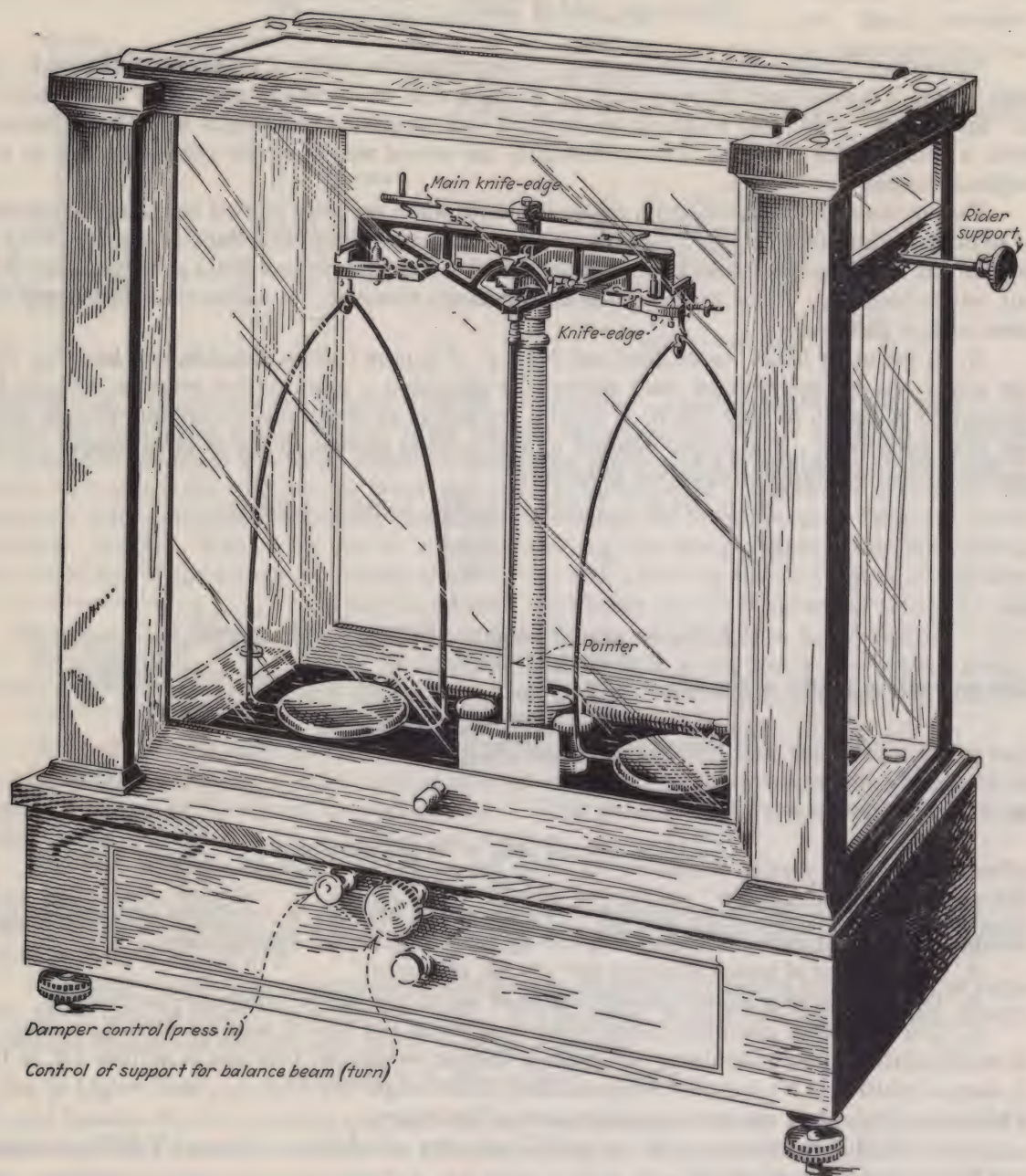


FIG. 5.—The accurate balance.

2. *Accurate Balances* (Fig. 5).—These are enclosed in glass cases and will weigh to 0.1 mg. or 0.0001 g., but unless advised by the instructor you will not be required to weigh with greater accuracy than is represented by 0.005 g.

To produce their great sensitivity, these balances are delicately constructed and naturally require very careful handling. The following general rules must *always* be observed.

- a. No load of over 100 g. must be placed on the balance.
- b. Never put any objects except those of metal, glass, or porcelain directly on the balance pan. Place other materials on a watch glass.
- c. Hot objects must never be placed in the balance case.
- d. Handle the weights with the forceps provided, do not use the fingers, and after weighing replace the weights in order in the box.
- e. When altering load or weights, make sure that the beam is supported, and when finished be sure the beam is raised and the balance case closed.

If the balance is out of order report the fact to the instructor. Do not attempt to make repairs yourself.

Procedure for Weighing on Accurate Balances.—Seat yourself directly in front of the balance. With the balance case closed, release the pans (damper control), and lower the beam gently on to the knife-edge so that the pointer swings over two or three scale divisions. Observe the mid-point of the swing. This is known as the “resting point” or “zero point” of the balance and should be within one division of the center of the scale. Now raise the beam, open the balance case, and place the object to be weighed on the left-hand pan. Place weights on the right-hand pan, starting with a large weight estimated to be near the weight desired and proceeding successively to the smaller weights. To determine whether any weight is too much or too little, lower the beam *slightly* and notice the direction in which the pointer moves. *Never* let the beam swing completely over to one side. When the point is reached at which the addition of 10 mg. causes the right-hand side to be too heavy, while without this weight the pointer swings to the right more than to the left, count and record the weights on the pans, estimating the number of milligrams to be added to produce a balance. Check your weight by counting the weights as they are replaced in the box.

For more accurate weighings, the instructor will advise you on the use of the rider.



SECTION A

PRINCIPLES OF CHEMISTRY

ASSIGNMENT 1

CONSTRUCTION OF APPARATUS

Glass Bending.—There are very few experiments that can be performed which do not involve the bending of glass tubing, so that the sooner the student becomes familiar with the technique of the process the more rapidly may he carry out his work.

In bending tubing, the main essential is that the inner bore of the bent tube be uniform throughout its entire length. If the walls collapse causing a restriction in the tube, it must not be used in the construction of any apparatus. The tube at such a bend is weak, and a breakage may result in a severe wound to the hand; or since the bore is diminished, the tube may become plugged, and an explosion result.

Always use a *fishtail* or a *wing-top burner* (Fig. 6) for heating tubing preparatory to bending, and use a small flame in order to avoid peaks where the temperature will be higher than that of the rest of the flame. Place the glass lengthwise in the flame, and revolve slowly, at the same time moving it gently parallel to the fishtail or wing-top burner, so as to extend the heated area about $\frac{1}{2}$ in. on each side of the flame. When the glass begins to melt as indicated by a *uniform yellow flame*, remove the tubing, and bend carefully. *Do not force*, and if sufficient bend is not obtained, reheat carefully as before and proceed as above until the correct angle is obtained.

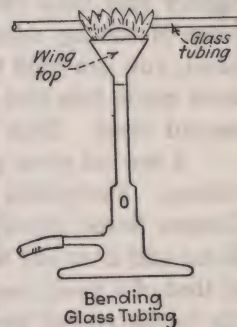


FIG. 6.—Wing-top burner.

EXPERIMENTAL

Take a few pieces of glass tubing (6 in. in length will be sufficient), and practice making a 45-deg. bend, a 90-deg. bend, and a complete curve. Keep on trying until you are sure you can repeat any of these without difficulty. Present your final efforts to the instructor for approval before continuing with the next assignment.

Boring Corks.—Before attempting to bore a hole in a cork, make sure that the cork will fit the apparatus in which it is to be used. The next step is to check the size of the glass tubing to be used against the cork borer. This precaution will ensure tight-fitting joints and may prevent the needless repetition of entire experiments.

Having determined the size of the cork and of the tubing, select a *good* cork and roll it several times in the cork roller. If such is not available, rolling with the foot, followed by rinsing will soften the cork so as to ensure a tight fit. The cork is then placed small end uppermost on a *firm* surface and is cut by turning the borer slowly with an even pressure. *Do not cut completely through*, but reverse the cork and bore from the other side to meet the original cut. In this manner clean edges are obtained at both ends of the cork.

If you should happen to spoil a cork, throw it into the waste jar. Never return used corks among the new ones.

Inserting Tubes into Corks, Etc.—Before attempting to pass a glass tube or rod through a cork or into rubber tubing, always "fire-polish" the ends. This is accomplished by holding

the end of the tube or rod against a hot flame (Fig. 7). Wetting the glass will aid in slipping the tubing through a cork or stopper. *Never press downward on glass in such a way as to allow the hand to be cut in the event of breakage.* If the tube is too short to permit its being grasped at the side, or if it has a bend in it, *always* protect the hand with a towel before exerting any pressure.

Ninety per cent of laboratory accidents are due to failure in observing this precaution.

Construction of a Wash Bottle.—One of the most useful pieces of equipment a chemist possesses is known as a "wash bottle." It is indispensable for washing precipitates from beakers into the filter and for washing the residue on the filter.

Materials Required:

- 500-ml. Florence flask
- Cork to fit above
- Glass tubing
- Short piece soft-rubber tubing



FIG. 7.—Fire-polishing.

Procedure.—Wash the flask with cleaning solution, followed by rinsing with water. Choose a cork that will fit your flask tightly and bore two holes in it to fit the glass tubing provided. Refer to Fig. 8, and bend a piece of tubing, adjusting the bend so that, when you hold the flask by the neck in your right hand, you can hold the glass tubing with the first and second fingers of the same hand. *After* you have made this first bend, pass the tube through one of the holes in the cork and then make the second bend. This allows of complete removal of water from the wash bottle.

A second piece of tubing is bent so as to form a straight line with the first bend in the other tubing. Fire-polish all ends. To make the tip, heat a short piece of tubing in the ordinary Bunsen flame (revolving as outlined for ordinary bending) and when molten remove from the flame and *draw out* slowly and evenly until the bore of the tubing has been diminished to the size of that of a medicine dropper. Allow to cool, and then cut at the center with a file. Attach the tip to the rest of the apparatus by means of a small piece of rubber tubing. When completed, the construction should be such that a student, while grasping the wash bottle, may direct a stream of water in any direction, by manipulating the tip with two fingers of the right hand, leaving the other hand free to hold a beaker, watch glass, etc.

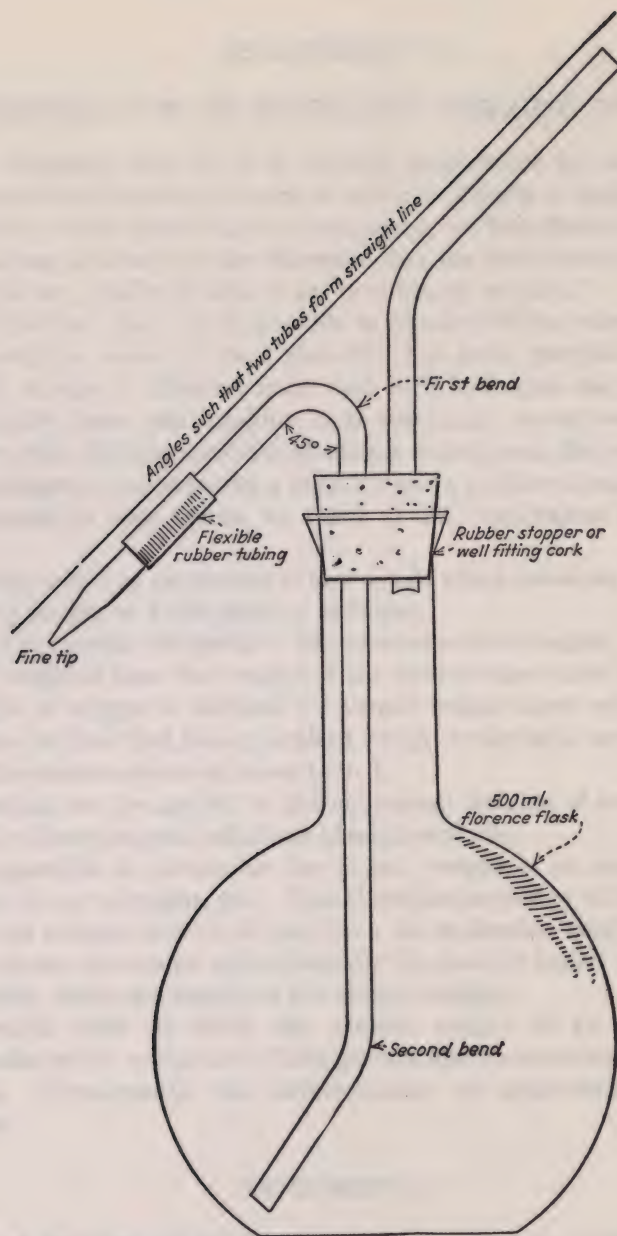


FIG. 8.—Construction of a wash bottle.

ASSIGNMENT 2

THE DETERMINATION OF EQUIVALENT WEIGHTS OF ELEMENTS

When elements combine, they do so in definite proportions by weight. Thus sulfur will combine with hydrogen in the ratio of 32 parts of sulfur to 2 parts of hydrogen and so on. When two elements combine to form more than one compound, we find there is also a definite relationship between the various amounts of the elements that combine (law of multiple proportions). These relative weights are usually spoken of as "combining weights."

It can be seen, however, that it is impossible to obtain definite values for comparison in the case of combining weights, since no fixed standard has been specified. Thus the combining weight of sulfur with oxygen is different from that with hydrogen and so on.

In order to simplify these relationships, it is customary to express combining weights in terms of combination with definite amounts of certain substances, the two most commonly used being oxygen and hydrogen as representing a negative and a positive element respectively. When combination is expressed in such terms, we speak of the "equivalent weight" rather than the combining weight.

Thus the equivalent weight of an element is that weight which combines with, displaces, or brings into reaction 8 parts of oxygen or 1.008 parts of hydrogen.

If the units used are grams we speak of the *gram-equivalent weight*.

The equivalent weight is thus that weight of the element associated with one valence. Thus the equivalent weight of oxygen is one-half its atomic weight since oxygen has a valence of 2. In the case of sodium we find that the equivalent weight is the same as the atomic weight, since sodium never exhibits valence states of other than 1.

This same reasoning can be applied to the equivalent weights of compounds as we shall see later when we come to discuss normal solutions (Assignment 20).

Usually it is impossible to determine the atomic weight of an element directly, since the element may be uni-, bi-, or trivalent, etc. It is therefore necessary to determine the equivalent weight or weights of an element first of all, and then the molecular weights of a great many of its compounds, before we can determine experimentally *the smallest weight ever occurring in one mole of any of its compounds*, which we accept as the atomic weight.

It is also essential that we know the atomic weight of an element before we can determine the formulas of its compounds from percentage composition data, as we shall see in another assignment. Consequently the determination of equivalent and atomic weights is extremely important.

EXPERIMENTAL

The Determination of the Equivalent Weights of Magnesium and Aluminum by Displacement of Hydrogen from an Acid.

Any metal above hydrogen in the electromotive series (see Appendix) will displace this element from dilute, non-oxidizing acids. Magnesium, being high in this series, reacts quite vigorously and completely with dilute hydrochloric acid. Consequently, if a weighed amount of magnesium ribbon is allowed to react with the dilute acid, it can only do so by replacing the hydrogen in definite proportion by weight. If the gas displaced is collected, it will represent the amount of hydrogen displaced by the weighed quantity of the metal.

Thus if 0.1 g. of magnesium is weighed out and the hydrogen liberated occupies a volume of 92.10 c.c. when calculated at standard conditions of temperature and pressure, 0°C. and 760 mm. of mercury, it is apparent that the equivalent weight of magnesium will be

$$\frac{11,200 \text{ c.c.}}{92.10 \text{ c.c.}} \times 0.1 \text{ g.} = 12.18 \text{ g.}$$

since by definition the gram-equivalent weight is that weight which displaces 1.008 g. (and consequently 11.2 l. under standard conditions) of hydrogen.

In experimental work, gases are commonly collected and maintained over water. The volume obtained will therefore represent that of a mixture of the hydrogen liberated and the water vapor present. It is essential therefore that we calculate the volume of the hydrogen alone. Knowing the barometric pressure and the temperature of the water, we can obtain (from Dalton's law of partial pressures) the pressure due to the hydrogen.

Barometric pressure = pressure due to hydrogen + pressure due to water vapor

or

$$P_{H_2} = P_{\text{total}} - P_{H_2O}$$

By applying Boyle's and Charles's laws and using the corrected pressure, it is possible to calculate the volume of hydrogen that has been displaced by the metal, in terms of standard conditions.

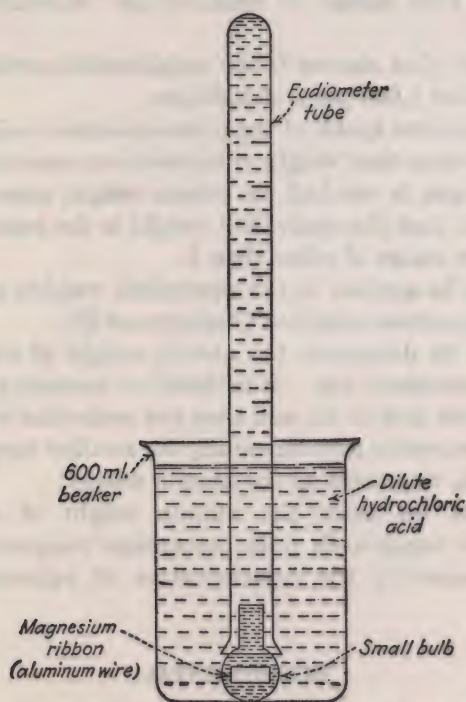


FIG. 9.—The equivalent weights of magnesium and aluminum.

Apparatus:

- 50-ml. eudiometer tube
- 600-ml. beaker
- Large cylinder
- Thermometer
- Glass tubing
- 250-ml. graduate

Materials:

Magnesium ribbon
Aluminum wire
Copper wire
Hydrochloric acid 1*N* and 6*N*
Emery cloth

Procedure. *Part A.*—Take a short length of glass tubing and seal the end in the burner flame. Blow the end out to form a small bulb somewhat larger than the end of the eudiometer tube, and when the glass is cold cut off the stem about $\frac{1}{2}$ in. above the bulb.

Clean between 0.03 and 0.04 g. of magnesium ribbon with emery cloth and weigh accurately, using the rider. Fold the strip accordion-wise and place it in the glass bulb, which is then completely filled with water. Place about 400 ml. of water in the 600-ml. beaker. Fill the eudiometer tube completely with 1*N* hydrochloric acid and, placing the thumb or finger over the end, invert the tube in the beaker of water. No air bubbles must be left in the tube. Now fill the beaker with water to within 1 cm. of the top.

With one hand raise the eudiometer tube sufficiently to permit the stem of the bulb containing the metal to be inserted. The tube is then lowered and allowed to remain until the magnesium has reacted completely.

Sealing the mouth of the eudiometer tube with your thumb, transfer it mouth downwards to a large cylinder of water and leave it for 10 min. At the end of this period read the barometric pressure, record the temperature of the water, and read the volume of gas in the tube when the level of water inside is the same as that outside.

Part B.—A similar experiment is now to be carried out using between 0.03 and 0.035 g. of aluminum wire weighed accurately. The weighed piece of aluminum is twisted around 2 in. of copper wire and the whole placed in the small glass bulb. In this case fill the eudiometer tube with the 6*N* hydrochloric acid.

TREATMENT OF DATA

1. Calculate the volume of hydrogen under standard conditions which was obtained in each experiment.
2. Calculate the equivalent weights of magnesium and aluminum.
3. Look up the corresponding atomic weights, and calculate the valences of the two metals from your results.
4. Write the equations for the reactions.

EXERCISES

1. What other metals would you suggest as being suitable for this experiment? What other acids?
2. Why is the collected gas kept over water for 10 min.?
3. Is it necessary that the levels of liquid inside and outside the eudiometer be the same when reading the volumes of the gases? What would be the effect of reading the volume when the level in the tube is (a) higher than, (b) lower than, the outside level?
4. Pure aluminum reacts rather slowly with dilute hydrochloric acid owing to the fact that an adhering layer of hydrogen forms on the metal surface and hinders further action. Explain how this is avoided by the use of the copper wire.
5. Does the copper take any part in the chemical reaction? Explain your answer.
6. Write the formulas for magnesium phosphate, magnesium hydroxide, aluminum sulfate, and sodium aluminate.

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ASSIGNMENT 3

THE DETERMINATION OF FORMULAS OF COMPOUNDS. GRAVIMETRIC METHOD

In Assignment 2 we determined the equivalent weights of elements that exhibit one valence state only and consequently form only one series of compounds in which the element has always a valence of +2 or of +3. Certain elements, however, such as iron, copper, mercury, etc., have more than one equivalent weight, thus permitting of the formation of more than one compound with the same elements (law of multiple proportions). Thus it often becomes necessary to distinguish between two compounds of one element, as, for example, oxides of iron.

In order to calculate the relative amounts of the constituents, we make use of the two units, the equivalent weight and the atomic weight. It is well to bear in mind that the equivalent weights and atomic weights, although sometimes of the same value, are nevertheless by definition entirely independent of one another. For whereas the former is *the weight of an element that will combine with a fixed unit*, the latter is *the relative weight of the atom compared to a fixed unit*. Thus the atomic weight of oxygen is 16, since the average weight of its atoms compared to that of those of hydrogen is in the ratio 16:1.008. On the other hand, the equivalent weight of oxygen is 8 since 8 parts of this element combine with 1.008 parts of hydrogen.

Analysis of a compound in question will indicate the proportions in which the elements are combined, and from these the fractions of atomic weights of each that are present can be calculated, provided, of course, that the atomic weights of the elements are available. The formula of the compound may then be determined.

Simplest and True Formulas.—Unless the molecular weight of the compound can be determined, our formula will represent only the simplest one we can write. For example, in the case of mercurous chloride, the percentage composition obtained from an analysis could be expressed accurately by either of the formulas HgCl or Hg_2Cl_2 . The molecular weights are different, and a knowledge of the molecular weight of the compound allows us to assign the latter formula as being the correct one.

Example.—An analysis of a compound shows it to be an oxide of iron. A quantitative determination on a sample weighing 15.90 g. indicated an oxygen content of 30.19 per cent. The percentage of iron in the sample was therefore 69.81. The atomic weights of oxygen and iron are 16 and 55.84, respectively. Consequently in 100 g. of the oxide the number of atomic weights of iron will be

$$\frac{\text{Percentage of Fe in sample}}{\text{Atomic weight of Fe}} = \frac{69.81}{55.84} = 1.25$$

and the number of atomic weights of oxygen will be

$$\frac{\text{Percentage of O in sample}}{\text{Atomic weight of O}} = \frac{30.19}{16.00} = 1.88$$

The ratio of the number of atomic weights of each element present is consequently 1.25:1.88 or 1:1.5.

However, since the number of atomic weights of each element present in one molecular weight must be a whole number, the simplest ratio possible will be 2:3 and hence the *simplest formula* of the oxide is Fe_2O_3 .

EXPERIMENTAL

The Determination of the Formula of an Oxide of Copper from Percentage Composition

Copper forms two oxides since it exhibits more than one valence. In order to determine the formula of the oxide under investigation, it is necessary therefore to analyse the compound quantitatively. This may be accomplished by heating a weighed portion of the oxide in a stream of hydrogen. The hydrogen reduces the copper to its elementary state by combining with the oxygen to form water.

The difference in weight of the sample before and after reduction represents the amount of oxygen in the original sample.

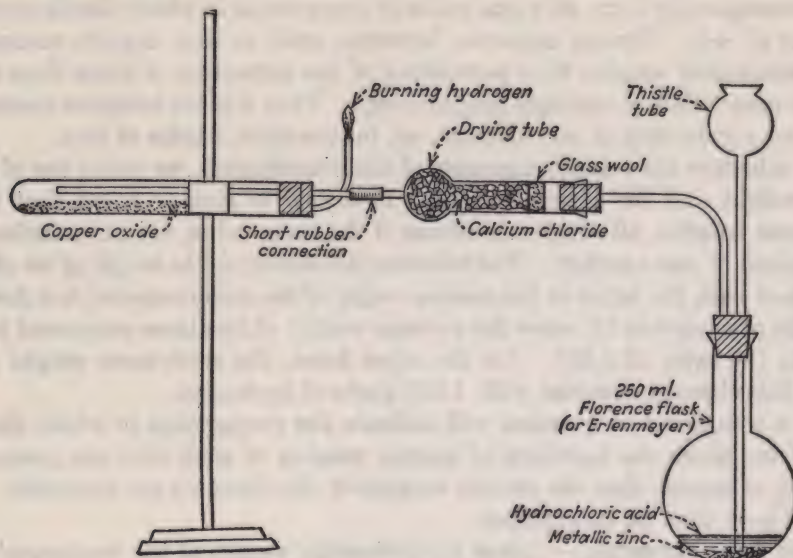


FIG. 10.—The formula of an oxide of copper.

Apparatus:

- 250-ml. Erlenmeyer or Florence flask with two-hole rubber stopper
- Thistle tube
- Hard-glass test tube fitted with two-hole stopper
- Drying tube
- Glass tubing
- Short piece of rubber tubing

Materials:

- Copper oxide
- Granular or mossy zinc
- Concentrated hydrochloric acid
- Calcium chloride
- Glass wool

Procedure.¹—Weigh a clean dry hard-glass test tube to within 0.01 g. by suspending it from the arm of the balance with the wire provided. (Do not remove this wire.) Insert carefully approximately 1.0 g. of the oxide of copper into the test tube and record the new weight. The difference between the two will represent the weight of the oxide.

By tapping the test tube gently, spread the oxide in a thin layer along the lower half of the test tube, and connect to an apparatus as shown in the diagram (Fig. 10).

¹ An alternative method is to draw out the closed end of the test tube into a narrow tip which is turned upwards. A single-hole stopper is then sufficient and the hydrogen is burned at the constricted end of the test tube.

Note.—Hydrogen, when mixed with air, is a violent explosive. Hence all stoppers, tubing, etc., must fit absolutely tightly. As a further precaution, wrap the generator in a towel. **Never** have a flame near the apparatus generating hydrogen unless it is being used. Care must also be taken to see that the glass tube delivering the hydrogen to the test tube does not touch the oxide. Any stoppage will result in an explosion. There is absolutely no danger if directions are followed closely.

A layer of zinc is placed in the bottom of the flask and covered with water, so that the thistle tube projects below the surface. When you are sure that the apparatus is tight, call the instructor and obtain his approval before continuing further.

Pour a little concentrated hydrochloric acid (20 ml.) through the thistle tube. Evolution of hydrogen takes place immediately, but the gas that first escapes from the delivery tube is a mixture of air and hydrogen and is explosive. All flames *must* be kept at least 3 ft. from the apparatus until the following tests have been made. Hold an inverted test tube over the delivery tube, thus collecting some of the escaping gas, and light it at the distant burner; then as quickly as possible light the gas issuing from the apparatus with the flame in the test tube. The jet must *never* be lighted by any other method. If the gas is a mixture there will be a slight explosion in the test tube, and hence no flame will be obtained. It is only when the hydrogen is pure that it will burn slowly enough to allow of the ignition of the gas at the jet. As long as the hydrogen burns at the jet with a quiet flame, the experiment may be continued.

The oxide in the tube is then gently heated with the flame of a wing-top burner. The temperature is gradually raised (but not to red heat) until the color of the contents of the tube has entirely changed. This should not require longer than 10 or 15 min. A steady stream of hydrogen must be maintained by adding more acid or zinc, when necessary. If it becomes necessary to disconnect the apparatus before the completion of the experiment, the air must once more be removed from the system, as was done formerly, before reheating the tube.

All traces of moisture are then carefully driven from the tube, the burner flame is *extinguished*, and the test tube allowed to cool with a current of hydrogen still passing. The test tube is now removed and held in a vertical position for a few minutes and then weighed on the same balance and with the same wire for suspension as formerly.

Return the calcium chloride to the container provided and, after filling the generator with water, pour the solution only, into the sink, washing down with water to reduce corrosion by the acid. The *zinc is not put into the sink*. Throw it into the waste jars.

TREATMENT OF DATA

1. From the weights observed, calculate the percentage composition of the copper oxide.
2. Determine from this and the atomic weights of copper and oxygen the simplest formula of the oxide.
3. What is the valence of copper in this compound?

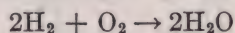
EXERCISES

1. What other valence does copper exhibit? Write the formula of the oxide in which copper has this valence.
2. For the same weight of copper as that obtained in the experiment, what would be the weight of a sample of the other oxide of copper?
3. Show from the equation for the experimental reaction that the reduction of the copper was accompanied by the oxidation of some other element.
4. Calculate the volume of hydrogen at 20°C. and 750 mm. required in the above experiment.

ASSIGNMENT 4

THE DETERMINATION OF THE FORMULAS OF COMPOUNDS. VOLUMETRIC METHOD

We have seen in the previous assignment that the formula of a compound can be obtained as a result of the experimental determination of its composition by weight. Another method of obtaining formulas is sometimes used which makes use of Avogadro's law, which states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. The *volumes* of two gases entering into combination with one another must then be in the same ratio as the *numbers of molecules* of the two substances which react. Thus since two volumes of hydrogen react with one of oxygen to form water, two molecules of hydrogen must react with one molecule of oxygen according to the equation



Since the molecules of most elementary gases consist of two atoms each, the ratio of the *volumes* will also be the ratio of the *numbers of atoms* reacting. This gives us at once the formula of the compound formed, or at any rate the simplest formula.

EXPERIMENTAL

The Determination of the Volumetric Composition and the Formula of Ammonia

One method of determining the composition of ammonia is to electrolyze a concentrated solution of ammonia, containing a little ammonium sulfate (*never* ammonium chloride since the violently explosive NCl_3 may be formed). The nitrogen collects at the anode and the hydrogen at the cathode.

In the present experiment we make use of an indirect method which does not involve the use of the electric current. One of the important chemical characteristics of chlorine is its affinity for hydrogen, whether the latter be in the free or combined state. Thus chlorine will remove the hydrogen from ammonia to form hydrochloric acid, leaving the nitrogen free. It is obvious that the volume of chlorine reacting will be equal to the volume of the hydrogen which formed the ammonia.

If then an excess of ammonia gas is mixed with a given volume of chlorine, all of the chlorine will react to form hydrochloric acid which will combine with the excess of ammonia to form ammonium chloride. The rest of the ammonia may now be removed by the introduction of a dilute acid, leaving the liberated nitrogen alone in the gas space. The volume of nitrogen being measured, we have the volumes of hydrogen and nitrogen which would unite to form ammonia, and thus the formula may be obtained.

Apparatus:

- Burette with glass stopcock
- Thistle tube
- 600-ml. beaker
- Chlorine generator
- Thermometer
- 100-ml. graduate

Rubber tubing
Rubber stopper

Materials:

Manganese dioxide and concentrated hydrochloric acid for chlorine generator
Concentrated ammonium hydroxide
Dilute sulfuric acid

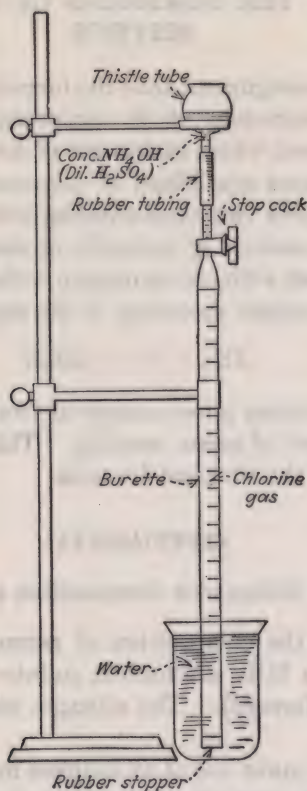


FIG. 11. The volumetric composition of ammonia.

Procedure.—Fill a 600-ml. beaker with water, and saturate with chlorine gas under the hood. Fill the tip of a burette with concentrated ammonium hydroxide by pouring a few cubic centimeters of the solution into the burette and opening the cock slowly. When this has filled, close the stopcock and rinse out the body of the tube thoroughly with water. Fill the burette with the chlorine solution and invert in the beaker of the same, connecting by means of a delivery tube to the chlorine generator. Displace the solution with chlorine gas and, when the tube is filled with chlorine, raise it somewhat until the mouth of the burette is just below the surface of the solution. Remove the delivery tube, and insert a previously selected, well-fitting rubber stopper into the mouth of the burette. Record the temperature of the solution in the beaker.

Clamp the burette as shown in the diagram (Fig. 11), the lower portion being maintained in a beaker of water. A short-stemmed thistle tube is connected to the tip of the burette as shown, by a short piece of tightly fitting rubber tubing.

Next, 3 ml. of concentrated ammonium hydroxide are added to the thistle tube and allowed to pass drop by drop into the burette. Do not allow all the ammonia to pass into the tube but maintain a little in the stem above the stopcock to prevent escape of any gas. Close the cock, remove the thistle tube, and rinse well with water. Shake down the fumes in the burette and then replace the thistle tube.

Add *cautiously* a few milliliters of dilute sulfuric acid to the thistle tube to neutralize the ammonia remaining in the stem of the burette, followed by the addition of 10 ml. of 6*N* acid (sulfuric acid) which is allowed to flow into the burette to neutralize the excess of ammonia. Retain a little acid in the stem to act as a seal.

Close the stopcock, and remove the thistle tube. Remove the burette from the stand, invert it several times to ensure complete reaction between the acid and ammonia, and then replace it and allow it to attain room temperature.

Making sure that the rubber stopper is tight transfer the burette to a large cylinder of water, remove the stopper under water, and leave the burette for 10 min. Then adjust the burette so that the level of liquid inside is the same as that of the water outside and paste a strip of paper on the burette to mark this point. Record the temperature of the water.

Drain out the solution and wash the burette with water. Now fill it completely with water, with the stopcock closed, and replace the stopper displacing a little water, so that no air is contained in the tube. This volume of water represents the volume of the chlorine originally used.

Remove the stopper and decant the water into a graduated cylinder. Record the volume.

With the stem of the burette downward, fill with water so that the level coincides with the bottom edge of the gummed paper. This volume represents the volume of nitrogen liberated during the reaction. Decant this water into a graduated cylinder and record this volume.

TREATMENT OF DATA

1. Calculate the volume which the chlorine would occupy at the final temperature of the experiment.
2. Deduce the volumetric composition and formula of ammonia.

EXERCISES

1. Write equations for all the reactions taking place in the experiment.
2. Why is it not necessary to reduce the observed gas volumes to those at standard conditions?
3. The gases measured were mixed with water vapor. Assuming that the gases were saturated with water vapor in each case, what difference does this make in the accuracy of the results?

ASSIGNMENT 5

DETERMINATION OF THE MOLECULAR WEIGHTS OF GASES

Avogadro's law gives us a means of calculating the relationship between the masses and volumes of gaseous products. From this law we obtain the *gram-molecular volume* or the volume occupied by 1 mole (molecular weight expressed in grams) and find it to be a constant value, *viz.*, 22.4 l. when measured at 0°C. and under a pressure of 760 mm. of mercury. Thus if 1 mole of a substance occupies this volume under these conditions, it is obvious that the converse must be true, *viz.*, that *the molecular weight of a gaseous substance will be the weight of 22.4 l. of that substance when it is measured under conditions prescribed above.*

It is not necessary to deal directly with such large volumes, since if 1 l. is weighed it is evident that multiplying this weight by 22.4 will give us the same result as if weighed directly. Similarly it is not necessary to determine the volume under standard conditions, since reduced volumes may be calculated from those obtained under experimental conditions by the application of the gas laws.

If a sample of an unknown gas having a volume of 50 ml. is weighed at room temperature (20°C.) and atmospheric pressure (750 mm.), the reduced volume under consideration is

$$50 \text{ c.c.} \times \frac{750}{760} \times \frac{273}{293} = \text{volume under standard conditions}$$

The weight recorded will be for this volume of gas, which may be then used in the calculation.

Since it is usually necessary to determine molecular weights as well as equivalent weights in order to arrive at accurate values for atomic weights, the determination of the former is of considerable importance.

EXPERIMENTAL

The Determination of the Molecular Weight of Oxygen

This is readily accomplished by heating a compound rich in oxygen to such an extent that part, or all, of the compound is decomposed. If the compound is weighed before and after heating and the volume of gas liberated collected and measured, the difference in weight of the compound will represent the amount of the oxygen liberated. This method obviates the necessity of weighing volumes of gases directly.

Apparatus:

- 500-ml. Florence flask with two-hole stopper
- 600-ml. beaker
- Hard-glass test tube with one-hole stopper
- Pinch clamp
- Thermometer
- Glass tubing
- Rubber tubing
- 250-ml. graduate

Materials:

Potassium chlorate

Procedure.—Set up an apparatus such as is shown in the diagram (Fig. 12), making sure that all joints are tight before continuing. When the apparatus has been constructed, remove the

hard-glass tube and weigh it accurately by suspending it from the balance arm by the wire provided for that purpose. Having recorded the weight, weigh out approximately 5.0 g. of potassium chlorate on the rough balances, place this in the test tube, and reweigh on the accurate balances.

The Florence flask and delivery tube (see diagram) are completely filled with water, and the clamp on the delivery tube is closed. Support the flask, and connect the test tube as shown. On opening the clamp now, no water should siphon out of the flask. If it does so, the stoppers are not tight fitting and must be changed before continuing. When there is no leakage from the delivery tube with the clamp open, place a dry 600-ml. beaker under the mouth of the delivery tube. The test tube is then gently heated until the gas is liberated.

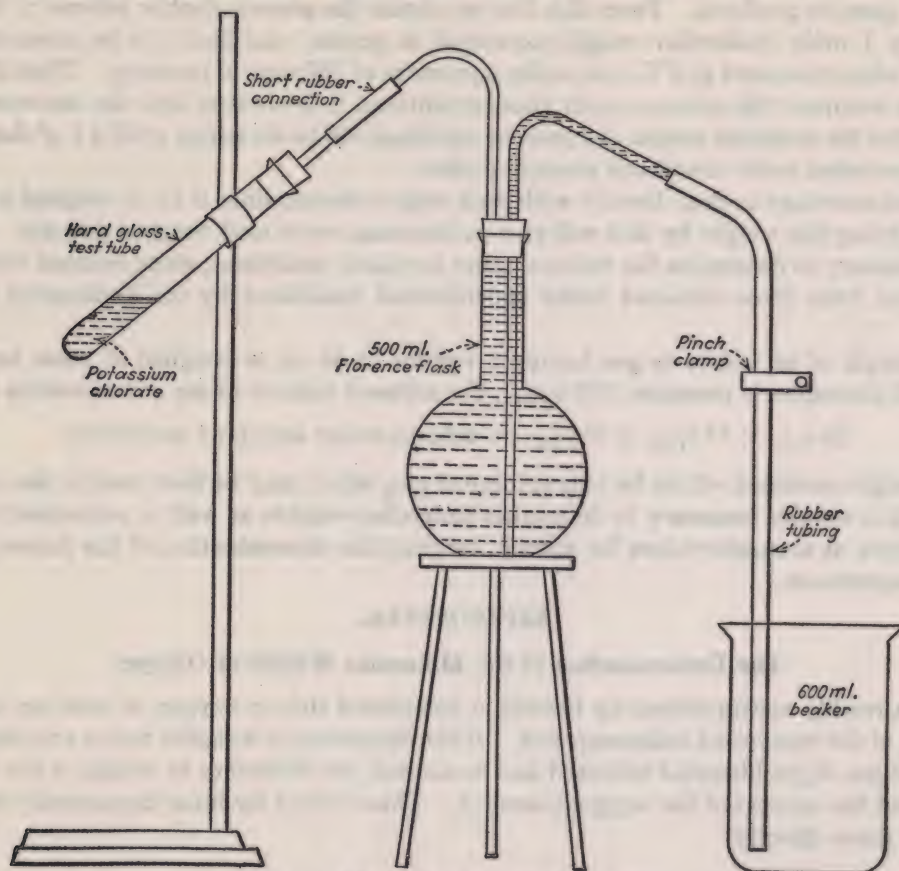


FIG. 12.—The molecular weight of oxygen.

Note.—Always heat solids at the surface, continuing the heating downward as the substance melts. This precaution prevents the formation of a hard crust in the test tube which might prevent the passage of the gas from the molten mass below it.

As the oxygen is liberated, raise the temperature until a steady stream of the gas is maintained. Water is displaced from the flask into the beaker, and care must be taken to keep the mouth of the delivery tube below the level of the water in the beaker. This will prevent air from being drawn into the flask as the flow of oxygen diminishes.

When between 350 and 400 ml. of water have been displaced and collected in the beaker, gradually diminish the heating, and allow the test tube to attain room temperature. During the cooling it is obvious that a certain volume of the water in the beaker will be forced back into the flask. As this is essential to the success of the experiment, the necessity of maintaining the mouth of the delivery tube well below the surface of the liquid in the beaker is evident. When the test tube is cool and no more water is being forced from the beaker, raise the beaker until the

level of the water inside the beaker corresponds to that within the flask. Close the clamp on the delivery tube, remove the test tube, and reweigh on the same balance and with the same wire as was used for the original weighing.

The volume of the water in the beaker is determined by careful measurement in a graduated cylinder and represents the volume of gas corresponding to the loss of weight of the potassium chlorate. Record the barometric pressure and the temperature of the water.

TREATMENT OF DATA

1. Taking the temperature of the gas as the same as that of the water displaced, calculate the volume of the oxygen under standard conditions. Take into account the fact that the gas was collected over water.

2. Obtain the weight of oxygen evolved, and calculate the molecular weight of oxygen.

EXERCISES

1. Write the equation for the reaction which took place.

2. Write down the values of the equivalent, atomic, and molecular weights of oxygen. Explain the relationship.

3. What weight of iron filings could be oxidized to Fe_2O_3 by 100 ml. of oxygen, collected over water at 20°C . and 770 mm. pressure?

ASSIGNMENT 6

THE DETERMINATION OF MOLECULAR WEIGHTS BY THE FREEZING-POINT METHOD

In Assignment 5 we learned how to obtain the molecular weight of a substance which could be obtained in the gaseous state, by application of the gas laws to observations of the pressure, temperature, volume, and weight of a sample of gas. In the case of non-volatile substances, however, this method cannot be applied, and it is necessary to find some other physical properties which depend upon the molecular weight. Fortunately we find that there is a great similarity between a substance in the gaseous state and in dilute solution. In the latter case the osmotic pressure plays the same part that the pressure does in the case of a gas. Thus to find the molecular weight of a dissolved substance, all that is necessary is to find that weight which, when contained in 22.4 l. of solvent at 0°C., exerts an osmotic pressure of 760 mm. Closely related to the osmotic pressure is the lowering of the freezing point of the solvent, due to the presence of the dissolved substance, and also the lowering of the vapor pressure and the raising of the boiling point.

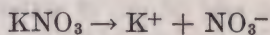
All these properties depend upon the number of moles of dissolved substance in a given quantity of solvent, *i.e.*, upon the concentration, and do not depend upon the kind of substance dissolved, so long as it is not ionized. It has been found that when one gram molecular weight of any non-ionized substance is dissolved in 1000 g. of water the freezing point is lowered from 0 to -1.86°C. As it is difficult to measure osmotic pressure accurately, it is more convenient to make use of one of these other related properties.

Thus we can readily measure the lowering of the freezing point and use this to calculate the molecular weight of a compound. For example, 30 g. of urea dissolved in 100 g. of water produce a lowering of the freezing point of 9.3°C. The molecular weight is then that weight of urea which in 1000 g. of water produces a lowering of 1.86° or

$$\text{Molecular weight} = \frac{1000}{100} \times 30 \times \frac{1.86}{9.3} = 60$$

Behavior of Electrolytes.—In the case of electrolytes—acids, bases, and salts—certain abnormalities appear. Thus the freezing point of 0.1 mole of sugar in 1000 g. of water is closely -0.186°C., while that of a similar solution of potassium nitrate is -0.330°C. The effect on the freezing point and other molal properties is much larger than would be expected on the basis of the number of moles present. This can best be explained by the assumption that the molecules of electrolytes break up in solution into smaller units, each of which behaves as a molecule as far as its effects on the physical properties of the solution are concerned.

Evidence from other sources confirms this conclusion and indicates that in the case of potassium nitrate the following process takes place:



The fact that the solution conducts the electric current shows that these part-molecules or ions are electrically charged. Since two ions are obtained for each molecule of potassium nitrate, it might be expected that the freezing point lowering should be $2 \times 0.186^\circ$ or 0.372° , instead of the measured value of 0.330° . This discrepancy was formerly explained by the assumption that ionization was incomplete, but this is no longer believed to be the case, and the difference is attributed to the electrical charges carried by the ions. The effect of these is to set up an interionic attraction or

drag between ions of opposite charge thus hindering their free motion and reducing their effect on the freezing point and other properties of the solvent. So with a salt like BaCl_2 which forms three ions, the freezing point lowering is somewhat less than three times the value which would be calculated on the basis of the molecular concentration.

EXPERIMENTAL

A. The Determination of the Molecular Weight of Sugar. B. Ionization of Sodium Chloride

In the present experiment the molecular weight of ordinary sugar (sucrose) is to be determined by measurement of the freezing point of a sugar solution. The solution is cooled to its freezing point by the addition of ice, which melts and abstracts heat from the solution until equilibrium is established between the ice and the solution, *i.e.*, until the freezing point of the solution is reached. The weight of sugar being known, the solution is then weighed, and the weight of water determined. Remember that the constant value of 1.86° for the freezing point depression refers to 1000 g. of *solvent* not of *solution*.

In comparison with this experiment, we shall also measure the freezing point of solution of sodium chloride, to determine the apparent molecular weight from the result.

Apparatus:

- Thermometer reading to -10°C .
- One 4-in. funnel
- 100-ml. graduate
- Two 250 ml. beakers

Materials:

- Sucrose, 30 g.
- Salt, 6 g.
- Ice

Procedure.—Thermometers frequently do not read 0°C . at the freezing point of water. This is due to errors in the manufacture and it is therefore necessary to calibrate your thermometer, by observing the position of the mercury when immersed in a mixture of water and ice, the temperature of which is exactly 0°C .

Fill a 250-ml. beaker with lumps of ice about the size of marbles. Wash the ice by covering it with distilled water, stirring with a glass rod, and pouring off the water. Wrap a towel around the beaker, then just cover the clean ice with distilled water, and insert the thermometer until the zero mark is just below the surface of the mixture. Stir the mixture slowly with the thermometer. When the thermometer indicates a constant temperature, note exactly the reading, estimating it to tenths of a degree. The reading thus made will be the freezing point of water, on your thermometer. Record this value.

Part A. The Molecular Weight of Sucrose.—Place the funnel on a filter stand and set a dry 250-ml. beaker under it. The funnel stem should just touch the inside wall of the beaker. Weigh out to the nearest 0.1 g. about 30 g. of sucrose. Place the sucrose in a 250-ml. beaker (not the one which is under the funnel) and add 50 ml. of water. Stir until the sucrose is dissolved. Now place your thermometer in the beaker and add pieces of washed ice about the size of marbles until the beaker is nearly filled, stirring slowly and carefully with the thermometer. Watch the thermometer as the temperature falls and read the lowest temperature reached, estimating this to the nearest tenth of a degree. Record this reading as the freezing point of the solution. The temperature should now start to rise slowly. As soon as a definite upward trend is noticed pour the contents of the beaker into the funnel, and collect the solution, now free from ice, in the beaker. After a few seconds remove the beaker and weigh it and its contents on the rough

balances to the nearest 0.1 g. Pour out the solution, dry the beaker, and reweigh. Record both weights.

Part B. Ionization of Sodium Chloride.—Carry out a similar experiment to that above, using 6 g. of sodium chloride in place of the sucrose. This should be weighed to the nearest 0.01 g. Record the results as before.

TREATMENT OF DATA

- A. 1. Calculate the weight of water present in the final sugar solution.
2. Calculate the molecular weight of sucrose from your data.
3. The formula of sucrose is $C_{12}H_{22}O_{11}$. Determine the exact molecular weight and compare your value with this.
- B. 1. Using the data obtained with sodium chloride, calculate a molecular weight as in Part A.
2. Compare this with the true molecular weight of sodium chloride and explain the discrepancy.

EXERCISES

1. In the above experiments why can we not take 50 ml. as the volume of water present at the freezing point?
2. What causes the temperature of the freezing mixture to rise before all the ice has melted?
3. In order to determine the molecular formula of a compound, what experimental information must be obtained in addition to the molecular weight?
4. How are exact molecular weights obtained?

ASSIGNMENT 7

RATES OF CHEMICAL REACTION. MEASUREMENT OF THE RATE OF A REACTION UNDER VARIED CONDITIONS

The rate at which a chemical reaction takes place is an important factor in the utilization of the process for industrial or laboratory purposes, as reactions show great differences in speed. Thus when we add a solution of an acid to that of a base, neutralization apparently takes place instantaneously, and the same applies to the majority of reactions which occur between substances in solution. On the other hand, the rusting of iron in moist air to form iron oxide is extremely slow and goes on over a period of days. The reaction between an active metal, such as zinc, and an acid like hydrochloric takes place vigorously, but the evolution of gas continues for some time before the zinc is used up, showing that the reaction proceeds at a fast but measurable rate. Thus under the same external conditions reactions show great differences in speed. These must be due to fundamental differences in the substances involved and are apparently connected with the structure of the molecules and of the atoms themselves.

However, if we change the external conditions, the rates of chemical reactions are also changed. We are all familiar with the fact that it is often necessary to heat the reacting substances in order to start vigorous reaction. For example, carbon at ordinary temperatures does not apparently combine with the oxygen of the air at all, but when carbon is heated to a high temperature the combination takes place very rapidly and we call it combustion.

Temperature is therefore one of the external conditions which influence rates of chemical reaction. Careful investigation has shown that many reactions which do not seem to be taking place at low temperatures are really taking place extremely slowly, and that the effect of raising the temperature is merely to increase the speed of the reaction to the point at which it can be readily observed. Practically all reactions are affected this way by change of temperature, and we find in general that the speed of a reaction is approximately doubled for every 10°C . rise in temperature. This is a large acceleration, and it can be seen why many reactions which give out heat reach almost the velocity of an explosion as the temperature of the reacting substances is raised by the heat of the reaction.

The explanation of this effect of temperature is to be found in the behavior of the molecules themselves. We picture the molecules of a substance in the gaseous or liquid state as having different speeds, some very slow and others extremely fast. These molecules are colliding with one another and changing their speeds continuously. At the same time the atoms which compose these molecules are vibrating back and forth, this vibration being sometimes increased and sometimes decreased as the molecule collides with other molecules. This energy of motion is apparently due to the heat which the substance contains. At any temperature there are a certain number of molecules whose atoms are vibrating so fast that they tend to break away from each other and combine to form new molecules, either by themselves or with the atoms of some other molecule for which they have an attraction. These molecules may then take part in chemical reaction. As we raise the temperature and put more heat into the substance, more of the molecules attain this critical or *activated* condition and hence the rate of the reaction is increased.

The *concentration* of the reacting substances is found to have a great influence on the rate of the reaction. This is to be expected since the more molecules there are in a certain space, the greater will be the number of collisions between them, and thus the greater the chance of two activated molecules' colliding and reacting. The rate of a reaction is found to be directly pro-

portional to the concentration of the reacting substances. Thus in the reaction between hydrogen and iodine vapor to form hydrogen iodide we have

$$\text{Rate} = k \times [\text{H}_2] \times [\text{I}_2]$$

In the case of gases, the concentration is directly proportional to the pressure, so that the greater the pressure of a gas, the greater will be its rate of reaction with some other substance.

In the case of solid substances, we cannot increase the concentration to an appreciable extent by compression. Here, however, the reaction must take place at the *surface* of the solid and we can increase the surface, for a given volume, by breaking up the solid into smaller particles. This is an effective way of increasing the rate of reaction of a solid substance and holds for some physical reactions as well; for example, a finely powdered solid will dissolve much more rapidly in a liquid than the same substance will when in large pieces.

Many reactions are found to increase in speed when there is present some foreign substance which we call a *catalyst*. Thus the decomposition of potassium chlorate to give oxygen is greatly accelerated by the addition of manganese dioxide, which is apparently unchanged in the course of the reaction.

EXPERIMENTAL

The Determination of the Effect of Temperature, Concentration, Exposed Surface, and Catalyst on the Rate of a Reaction

The reaction chosen is one which takes place at a convenient rate at room temperature, *viz.*, the displacement of hydrogen from an acid by the active metal zinc, and the rate is to be measured by the volumes of hydrogen liberated at certain intervals of time.

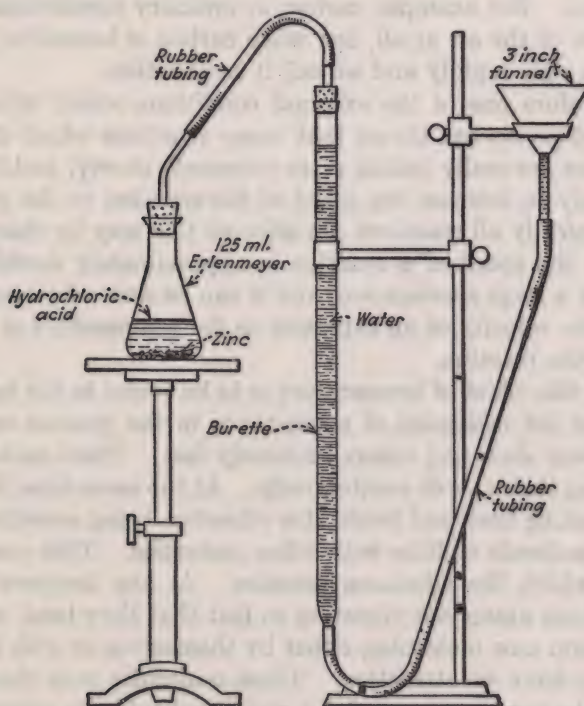


FIG. 13.—The rate of a reaction.

Apparatus:

- 50-ml. burette fitted with one-hole stopper
- 125-ml. Erlenmeyer flask with one-hole stopper
- 400-ml. beaker

3-in. funnel
Thermometer
Watch
Rubber and glass tubing
100-ml. graduate

Materials:

Zinc, granular
Zinc, powdered
Hydrochloric acid, 6*N* (desk reagent)
Copper sulfate, *N*/40 solution

Procedure.—*Make all your weighings at the beginning of the experiment.* Weigh out to the nearest 0.01 g. *three* portions of granular zinc of exactly 0.5 g. each and *two* portions of powdered zinc, also 0.5 g. each.¹

Part A. Effect of the Concentration of the Acid.—Set up the apparatus as shown in the diagram (Fig. 13). Fill the burette with water by pouring through the funnel until the water stands at the zero mark on the burette and just reaches to the top of the stem of the funnel when the burette top is open. Support the funnel at this height.

Place in the Erlenmeyer flask 50 ml. of 3*N* hydrochloric acid made by diluting the desk reagent with an equal volume of water.

You are now ready to start the reaction. *Quickly* pour one portion of powdered zinc into the Erlenmeyer flask, taking care that none sticks to the sides above the acid, and immediately insert the stopper. The water in the burette will be depressed to a small extent owing to air being forced in by the insertion of the cork. Read the water level *immediately* and record the time. At the end of 15 sec. adjust the water levels in burette and funnel to equality, and read the volume of gas which has entered the burette. Make similar observations at each succeeding quarter-minute until 50 ml. of gas have been collected. Record your data in the form of a table with time in one column and cubic centimeters in the other.

Now make a similar run, using the second portion of powdered zinc but having 50 ml. of 1.5*N* hydrochloric acid in the flask instead of the 3*N* acid. Take readings *every minute* in this case, and stop when 30 ml. of gas have been collected. Record the data as before.

Part B. Effect of the Surface of the Metal.—Carry out a similar experiment using a portion of granular zinc and 3*N* acid. Take readings of volume every minute up to 30 ml.

Part C. Effect of Temperature.—We will now compare the rate obtained in Part B at room temperature with the rate at a higher temperature, approximately 50°C. In this case use a portion of *granular* zinc, but make the following changes: after you have set up the apparatus, place in a large beaker enough water so that the mixture in the Erlenmeyer flask will be completely surrounded by water when the flask is immersed in the beaker. Heat the water to about 55°C. and set the flask in it. Add 25 ml. of 6*N* hydrochloric acid. Now heat 25 ml. of water to boiling and mix it with the hydrochloric acid in the flask. Now add the zinc and connect as before. Take readings every *half minute*, collecting in this case 50 ml. of gas.

Part D. Effect of the Presence of a Catalyst.—Carry on an experiment identical with that in Part B except that the acid solution is to be made by adding 25 ml. of copper sulfate solution to 25 ml. of 6*N* acid. Record the volume of gas liberated at *half-minute* intervals up to 50 ml. Allow the reaction in the flask to go to completion, then separate the solid product which remains. See if you can identify it.

¹ Sufficiently accurate results may be alternatively obtained by measuring out the zinc samples in a small spatula or spoon of such size that one level spoonful is approximately 0.5 g.

TREATMENT OF DATA

1. Plot all your results on a sheet of graph paper, using as ordinates the volume of gas observed, and as abscissas the time recorded. Mark each curve so as to connect it with the corresponding experiment.
2. Read off from your graph the time taken in each experiment for 25 ml. of gas to collect, and record these data in the form of a table.
3. By comparison of the figures obtained in Ques. 2, draw conclusions as to the effect of concentration, of surface, of temperature, and of a catalyst on the rate of the reaction.

EXERCISES

1. What is the solid product left suspended in the spent liquid in Part D? Write the equation for the reaction by which it was formed.
2. Which substance, the solid product or the added cupric sulfate, is the catalyst? Why?

SECTION B

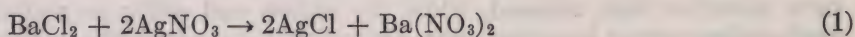
PREPARATION OF ELEMENTS AND COMPOUNDS

ASSIGNMENT 8

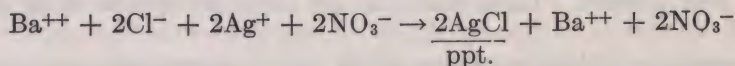
OXIDATION-REDUCTION REACTIONS. PREPARATION OF CRYSTALLIZED COPPER SULFATE, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

There are two main groups of inorganic chemical reactions: those in which the valences of the elements involved undergo no change and those in which there is a valence change on the part of some of the elements entering into the reaction.

Double-decomposition Reactions.—To the first class belong the double-decomposition or metathetical reactions. Here an interchange of ions takes place as in the reaction between two salts; *e.g.*,

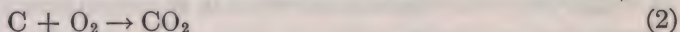


or



the reaction taking place owing to the tendency of the silver and chloride ions to form the little-soluble compound silver chloride. Note that no change of valence has been experienced by any of the elements or radicals involved.

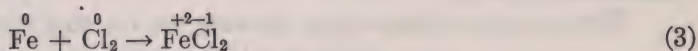
Oxidation-reduction Reactions.—In the second class we find reactions such as those of combustion or oxidation of substances by means of molecular oxygen; *e.g.*,



The carbon exerting no valence in the free state has been changed to a state in which its four valence bonds are in use. Since we consider oxygen as having a negative valence of 2, we may say that the valence of carbon has changed from 0 to +4 in this reaction.

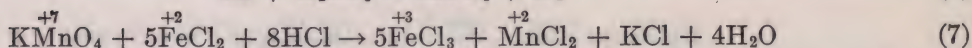
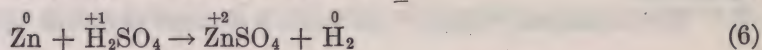
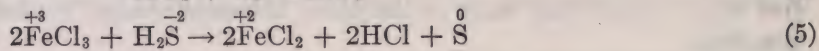
The term oxidation, however, is not restricted in application to reactions in which oxygen takes part but refers in general to the *increase of valence* which an element undergoes.

Thus in the reaction



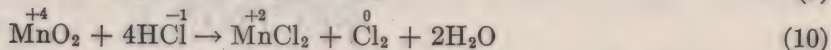
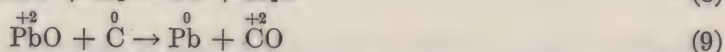
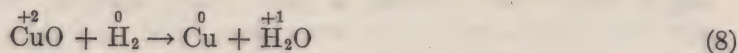
the iron has been as truly oxidized as was the carbon in the previous example.

Other examples of oxidation are:



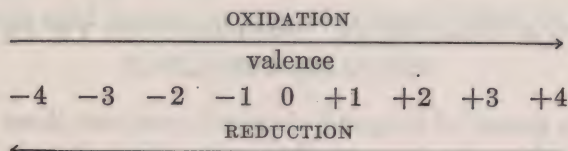
Note that as in Eq. (5) a valence change from a minus value to zero is equivalent to an increase in positive valence.

The term *reduction* signifies the opposite to oxidation and therefore means *decrease in valence* as in the examples:



In the last example we note that a change of valence from 0 to -2 is equivalent to a decrease in positive valence.

These relationships can be represented by the following diagram



On looking over the examples given, we note the important fact that each reaction involves *both* oxidation and reduction processes. Thus in Eq. (2) the valence of oxygen drops from zero to -2 , while in Eq. (5) iron changes in valence from $+3$ to $+2$, a decrease. These elements have therefore been reduced, while the carbon and sulfur respectively are oxidized. This is characteristic of all reactions of this type, *oxidation of one element being always accompanied by reduction of some other element*. These reactions are therefore spoken of as *oxidation-reduction reactions*.

Balancing Equations.—Equations representing oxidation-reduction reactions are frequently more complex than those of double decomposition and cannot in general be balanced by inspection or by trial. By the application of a few simple rules, however, the most complicated of such equations can be readily completed with the least expenditure of time and effort.

To tabulate these rules:

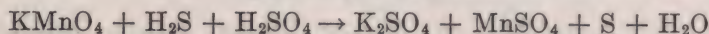
I. The valence of an element in the free state is to be taken as 0.

II. Only *two* elements involved in the reaction will change valence, one increasing, the other decreasing, its valence.

III. The total valence increase must be numerically equal to the total valence decrease. That is, if one element increases its valence by 2 while the other is decreased by 1, twice as many atoms of the second element as of the first will be involved.

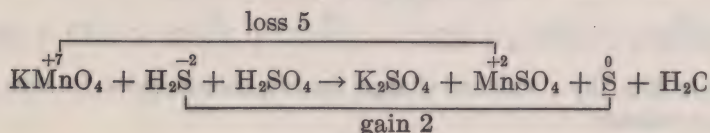
The application of these rules to a specific example will make the process clearer. Let us take the reaction between potassium permanganate and hydrogen sulfide in the presence of dilute sulfuric acid.

The equation is first set up showing the reacting substances and the products:

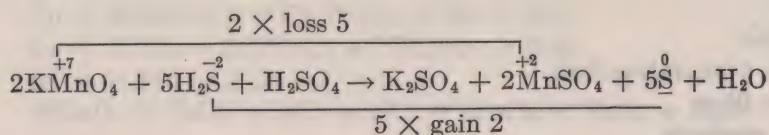


The two elements whose valences change are then noted and the valences marked. Here Mn changes from $+7$ in KMnO_4 to $+2$ in MnSO_4 , and S changes from -2 in H_2S to zero in the free state. Note that none of the other elements change valence although they may change positions.

The numerical values of the valence changes per atom are then marked:



These valence changes are then equalized. We multiply the number of Mn atoms by 2 and the number of S atoms by 5, so that the total valence decrease, 10, is equal to the total valence increase. This gives the coefficients for KMnO_4 , MnSO_4 , K_2SO_4 , H_2S , and S:



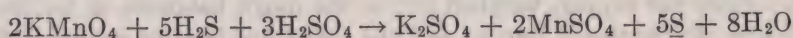
The coefficients for H_2SO_4 and H_2O can now be readily determined:

One SO_4 radical for K_2SO_4 .

Two SO_4 radicals for 2MnSO_4 , therefore $3\text{H}_2\text{SO}_4$ required.

Eight oxygen atoms left from 2KMnO_4 therefore $8\text{H}_2\text{O}$ will be formed.

The balanced equation is therefore



The balancing is verified by checking the number of hydrogen atoms on each side.

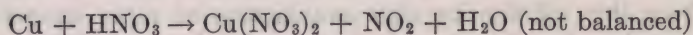
The above method is by no means the only one which can be used for balancing oxidation-reduction equations but its usefulness and simplicity commend it highly.

EXPERIMENTAL

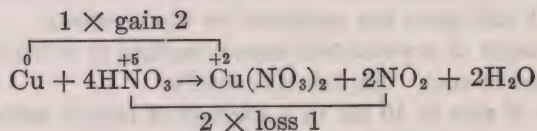
As an example of an oxidation-reduction process, the preparation of copper sulfate from metallic copper is to be carried out.

Since copper is placed below hydrogen in the electromotive series (see Appendix), it is not possible to prepare this compound by the displacement of hydrogen from sulfuric acid. On the commercial scale, copper sulfate is prepared by allowing dilute sulfuric acid to drip slowly over copper scrap exposed to the air. The oxygen of the air reacts with the copper to form copper oxide, which is then attacked by the acid to form copper sulfate and water. This is a slow process, however, and in the laboratory we make use of a more active oxidizing agent than free oxygen.

Copper reacts vigorously with nitric acid owing to the tendency of this acid to change to compounds in which nitrogen has a lower valence. Thus with concentrated acid:

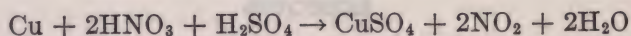


Here copper has been oxidized at the expense of nitrogen, which has decreased in valence from +5 to +4 and has therefore been reduced. This equation can be readily balanced by the method given above.



It must be noted that in addition to the 2HNO_3 required to provide the valence change, an additional 2HNO_3 is required to form $\text{Cu}(\text{NO}_3)_2$, the nitrogen in this case suffering no change of valence.

If now we treat metallic copper with a mixture of nitric and sulfuric acids, the reaction is as follows:



Copper sulfate crystallizes from solution with five molecules of water per molecule of salt, forming the blue hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which is commonly known as "blue vitriol."

The process of crystallization is described in the Introduction and this section should be reviewed before starting the experiment.

Apparatus:

Iron dish
100-ml. evaporating dish
Suction filter
50-ml. graduate

Materials:

Copper turnings, 10 g.	Concentrated sulfuric acid
Concentrated nitric acid	Pieces of copper and zinc
Dilute sulfuric acid	

Procedure.—Place the copper, weighed out on the rough balances, in the iron dish and heat vigorously until any oily matter is burned and the metal has become coated with a layer of the black oxide. While this is taking place, calculate the volumes of nitric acid and sulfuric acid required to react with 10 g. of copper according to the equation above. Concentrated nitric acid is 16*N* and dilute sulfuric 6*N*.

When the copper is cool, transfer it to the evaporating dish and place it *under the hood*. (NO_2 is poisonous and corrosive!) Add the calculated quantities of both acids. Warm the mixture carefully, taking care not to boil it, and allow the reaction to continue until the copper has dissolved. If at the end of 20 min. there still remains some of the copper, pour off the solution into a beaker and add 10 ml. of the acid mixture to the residue in the dish, heating as before.

When the copper is all dissolved, filter the hot solution, using a suction filter, and then cool the filtrate rapidly, stirring meanwhile to aid the formation of crystals. These should be in the form of a crystal meal. Decant the mother liquor and evaporate it to about 15 ml. On cooling, a second crop of crystals will be obtained. Decant, and discard the mother liquor which will contain soluble impurities as well as a small part of the copper sulfate.

Combine the two crops of crystals and dissolve them in an equal weight of water with heating. Place the solution in the evaporating dish and allow it to cool to about 35°C. Add one or two small crystals of copper sulfate obtained from the side shelf, as seed crystals, cover the dish, and set it away.

When crystallization has taken place, decant the mother liquor. A further crop of crystals may be obtained from this solution by slow evaporation at room temperature. Spread the product on a paper towel to dry, then transfer to a previously weighed dish, and weigh.

EXPERIMENTS

1. Heat a few pieces of metallic copper with about 2 ml. of concentrated sulfuric acid in a crucible. Note the result and write the equation for the reaction.
2. Heat a small quantity of crystallized copper sulfate in a crucible until the color change is complete. Let the crucible cool. Explain the results.
3. Add a small piece of zinc to 10 ml. of a solution of copper sulfate. Boil the solution and note the change in its appearance. Write the equation.

TREATMENT OF DATA

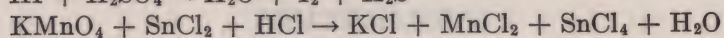
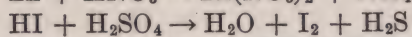
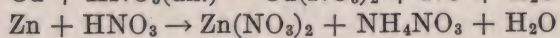
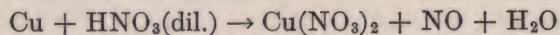
From the equation for the preparation of your product calculate your percentage yield on the basis of the weight of copper used.

EXERCISES

1. What is the purpose of cooling the original solution rapidly with stirring? Why is the final solution cooled slowly?
2. What happens to soluble and insoluble impurities in the above preparation?

3. Where in this preparation was there a saturated solution? An unsaturated solution? A supersaturated solution?

4. Balance the following equations:



ASSIGNMENT 9

UNIVALENT COPPER COMPOUNDS. PREPARATION OF CUPROUS CHLORIDE, CuCl

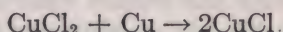
Copper, along with silver and gold, forms a subgroup of the alkali family in the Periodic Table. The valence assigned to this group is +1 corresponding to the single electron which exists in the outer shell of these atoms, and which is readily removed with the formation of ions. Copper is rather exceptional in that its stable valence state is +2, a second electron having been removed. Gold also shows an irregularity, having a stable valence of +3.

Copper, nevertheless, may exist in the valence state +1, cupric compounds undergoing reduction to cuprous under various conditions. The latter, however, readily revert to the higher and more stable valence compounds even as a result of oxidation by atmospheric oxygen. The cuprous compounds, therefore, are stable only in contact with some reducing agent.

In the lower valence state, copper shows some interesting similarities to silver. Thus cuprous chloride like silver chloride is insoluble in water but reacts with excess of chlorides or hydrochloric acid to form the complex ions CuCl_2^- and CuCl_3^- . Cuprous salts, like cupric and silver salts, react with ammonia to form complex ammonia salts.

EXPERIMENTAL

Cuprous chloride may be prepared by the interaction of cupric chloride and metallic copper according to the equation



In the absence of any other reagent, however, the reaction soon stops, due to the insolubility of CuCl which forms an impervious coating over the copper. This difficulty may be avoided by carrying on the reaction in the presence of concentrated HCl, which forms with CuCl the complex acids HCuCl_2 and H_2CuCl_3 , which are soluble and hence do not interfere with the progress of the reduction. After the completion of the reaction, the solution is poured into an excess of water, when the complex compound is decomposed and CuCl precipitated. As the moist product is readily oxidized by the air, care must be taken to dry the cuprous chloride rapidly.

Apparatus:

- 250-ml. flask
- 2-l. bottle (Winchester)
- Suction filter
- Thermometer
- 50-ml. graduate

Materials:

- Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 20 g.
- Copper turnings, 10 g.
- Concentrated hydrochloric acid
- Alcohol (denatured)
- Dilute ammonium hydroxide
- AgNO_3 solution

Procedure.—Dissolve the cupric chloride in 50 ml. of water and place the solution in the flask. Add 50 ml. of concentrated hydrochloric acid and the copper turnings and then warm the mixture to about 80°C. Continue to heat over a small flame, but do not boil it. The green color will gradually disappear and the solution take on a deep brown shade. Continue the heating for 10 min. after this has taken place, then test for complete reduction by pouring about $\frac{1}{2}$ ml. of the solution into a test tube and adding water. White cuprous chloride will be thrown down, and the solution above should show practically no blue color due to cupric ions. (Save the cuprous chloride thus formed and unite it later with the main bulk of the product.) Continue the heating until a satisfactory test is obtained. Decant the solution into 1 l. of cold water contained in the 2-l. bottle, leaving the residue of metallic copper behind. Wash this residue with 10 ml. of concentrated hydrochloric acid and pour this into the large bottle. Stir up the contents of the bottle, allow the cuprous chloride to settle out, then pour off most of the liquid. Now transfer the precipitate with the remaining solution on to a suction filter, rinsing out the last portions with a small amount of water.

As soon as the liquid has run through the filter, disconnect the suction tube and add 10 ml. of alcohol to the precipitate in the filter. Stir this carefully; then again apply suction. Repeat with a second 10-ml. portion of alcohol.

Tear off the upper part of the filter paper and spread the rest of the paper and precipitate out on a paper towel placed in a dish which is warmed by a small flame. When the cuprous chloride is thoroughly dry, transfer it to a dry corked test tube and weigh the product, which should be pure white.

EXPERIMENTS

1. Place about 2 g. of cuprous chloride in a test tube and fill the test tube completely with dilute ammonium hydroxide. Cork tightly, allowing no air to remain inside, and shake until the salt dissolves. Now pour the solution into a 250-ml. flask and cork this tightly. Shake the flask for 3 min., then invert and place its mouth under water, and remove the cork. Estimate the volume of gas remaining in the flask and explain what has taken place.

2. To 2 ml. of silver nitrate solution add concentrated hydrochloric acid drop by drop, and then in excess. Note the results. Pour the solution into 100 ml. of water. What happens? Write equations for all reactions taking place.

TREATMENT OF DATA

Calculate the percentage yield of cuprous chloride obtained on the basis of the weight of cupric chloride used.

EXERCISES

1. Write all the equations for the reactions occurring during this preparation.

2. The compound formed by the action of ammonia on cuprous chloride has the formula $\text{Cu}(\text{NH}_3)_2\text{Cl}$ and is colorless in solution. How do you account for the color changes observed in the experiment above?

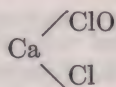
3. From the results of Experiment 2 state three properties which are common to silver ions and to cuprous ions.

ASSIGNMENT 10

TYPES OF SALTS. PREPARATION OF A DOUBLE SALT, CHROMIC ALUM, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

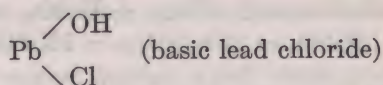
In Assignments 8 and 9 the student becomes acquainted with examples of simple salts, *i.e.* those which consist of a metallic ion combined with the radical of one acid. There are, however, several other types of salts which are of considerable importance, chief among which are the *mixed salts*, *basic salts*, *hydrogen salts*, *double salts*, and *complex salts*.

Mixed Salts.—When we have one metallic ion attached to two different acid radicals, we speak of the salt produced as being a mixed salt; *e.g.*,

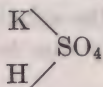


The salt in this case is that of both hydrochloric and hypochlorous acids.

Basic Salts.—These salts may be considered as resulting from the incomplete neutralization of the hydroxyl groups of bases. Consequently, the resulting salt contains one or more of these groups together with the acid radical; *e.g.*,

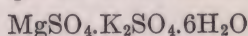


Hydrogen Salts.—Similarly salts may contain part of the hydrogen of the acid; *e.g.*,

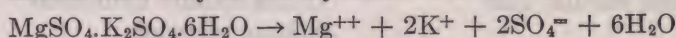


Double Salts.—Certain salts have the property of crystallizing out together in the same crystal, apparently losing their individual identities in so doing. The resulting substance is spoken of as a “double salt.”

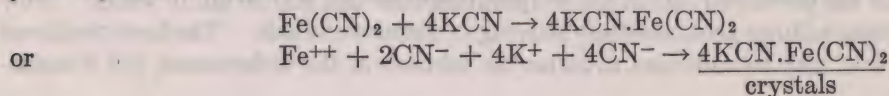
Thus if solutions of MgSO_4 and K_2SO_4 are mixed and gently evaporated until crystallization is effected, the crystals obtained correspond to the molecular formula



and this substance is a definite compound. On redissolving these crystals, ionization takes place and tests will show the presence of the Mg^{++} , K^+ , and SO_4^- ions in the resulting solution. Solution of a double salt therefore yields the ions from which it was originally obtained, and hence we meet with double salts only in the crystalline state.

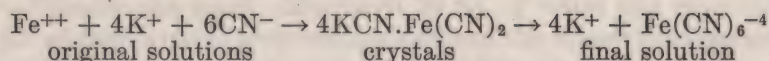


Complex Salts.—Certain other salts, when their solutions are mixed and evaporated, also yield crystals in which the two original salts are combined in the same crystal; *e.g.*



Upon redissolving this salt, however, and testing for the Fe^{++} ion and the CN^- radical, it is found that they are apparently no longer present as such in the solution, but that we now have K^+ ions and a new radical, $\text{Fe}(\text{CN})_6^{-4}$.

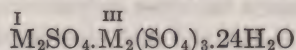
The reaction may be represented as follows:



When the crystals produced from two salts do not yield the original ions from which they were formed, we differentiate between these and double salts by naming them *complex salts*, because they furnish complex ions to the solution.

EXPERIMENTAL

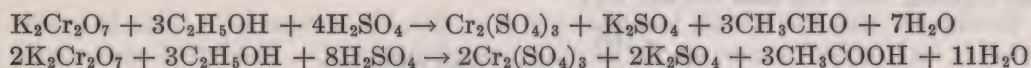
The *alums* consist of a series of isomorphous double salts of the general formula



where M and M are univalent and trivalent metals respectively. These salts form octahedral crystals, and large and perfect specimens may in many cases be obtained. Ordinary alum is a double sulfate of potassium and aluminum, whereas in chromic alum the trivalent metal is chromium instead of aluminum.

All chromium compounds are prepared originally from the naturally occurring chromite $\text{Fe}(\text{CrO}_2)_2$ (see Assignment 16). In the present preparation we start with potassium dichromate, the chromium being first reduced from a valence state of +6 to one of +3 in the presence of sulfuric acid, which forms the sulfates of potassium and aluminum.

As a reducing agent ethyl alcohol is used, itself being oxidized to acetaldehyde CH_3CHO —a substance that can be recognized by its penetrating odor—and to acetic acid CH_3COOH :



The alum may then be crystallized in large and beautiful deep purple crystals.

Care must be exercised, however, not to allow the temperature of the solution to rise above 40°C. during the preparation, for above this point the solution changes from purple to green, and crystals of alum will not form. This is apparently due to the formation of a complex ion containing chromium.

Apparatus:

4-in. evaporating dish
Thermometer
Mortar and pestle
50-ml. graduate
Suction filter

Materials:

$\text{K}_2\text{Cr}_2\text{O}_7$, 20 g.	Ice
Concentrated sulfuric acid	Dilute sodium hydroxide
Alcohol	Sodium peroxide

Procedure.—Weigh out on the rough balances 20 g. of potassium dichromate, and pulverize this in a mortar. Place the powdered salt in the evaporating dish and add 80 ml. of water. Now add 20 ml. of concentrated sulfuric acid, carefully stirring to dissolve the salt. The heat produced by the addition of the acid may be sufficient to cause the solution of the dichromate, but if necessary heat the mixture.

Allow the solution to cool to 30°C., meanwhile measuring out 15 ml. of alcohol in a graduate, then add the alcohol drop by drop, stirring constantly with the stem of a thermometer. When the temperature begins to rise, place the dish in a pan of ice and water, and add the rest of the

alcohol slowly, endeavoring to keep the temperature below 35°C. If the temperature starts to rise above 40°C., drop a small piece of ice *directly into* the solution.

When all the alcohol has been added, allow the solution to cool completely in the ice-water bath. The alum should separate in the form of a crystal meal. Collect the crystals on a suction filter, and redissolve them in about 50 ml. of water, warming to 40°C.

Make sure that no particles are left undissolved, add several seed crystals from the side shelf, and set the solution aside to crystallize for several days.

Remove the crystals and dry them by wrapping in filter paper. Weigh and record the weight.

EXPERIMENTS

1. Devise a test for the presence of Cr^{+++} ions in solution, and apply it to a solution of a little chromic alum in 10 ml. of water. What conclusion can be drawn as to the behavior of chromic alum in solution? Write the ionic equations.

2. Dissolve a little chromic alum in a few cubic centimeters of water and add an excess of sodium hydroxide. Add about $\frac{1}{2}$ ml. of solid sodium peroxide and shake the mixture. What is formed?

TREATMENT OF DATA

From the equations given above, calculate your percentage yield of chromic alum, based on the weight of potassium dichromate used.

EXERCISES

1. Name two other substances which might serve as reducing agents in place of alcohol. Write the equations.

2. Define an isomorphous substance and a double salt. Give another example of each besides chromic alum.

3. Name three other elements or radicals which could replace (a) potassium, (b) chromium, to form crystals isomorphous with chromic alum.

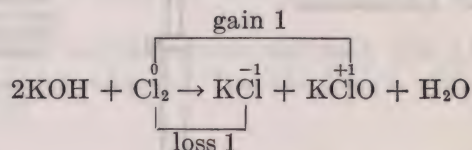
ASSIGNMENT 11

THE OXYGEN COMPOUNDS OF CHLORINE. PREPARATION OF POTASSIUM CHLORATE, KClO_3 , AND POTASSIUM HYPOCHLORITE, KClO

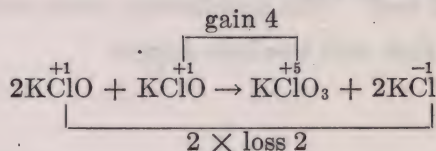
Molecular chlorine is one of the most active oxidizing agents we have, attacking almost all the other elements in the periodic system. Chlorine may enter into combination in a number of ways owing to its ability to assume valence states of -1 , 0 , $+1$, $+3$, $+5$, and $+7$. In its lowest valence, chlorine is a strong non-metal and thus forms very stable binary compounds with metals. When acting electropositively, we find the most stable compounds those in which the maximum valence is evidenced. Elementary chlorine may therefore be either oxidized or reduced. Those compounds in which the element exhibits a positive valence are powerful oxidizing agents, owing to the tendency of the chlorine to return to the negative condition and in so doing to lose valence.

The oxygen compounds of chlorine with sodium or potassium afford excellent examples of the various valence states of the element, *viz.*, KClO , KClO_2 , KClO_3 , and KClO_4 . For some reason chlorine appears to avoid, if possible, a valence of $+3$, so that the compounds usually met with are those exhibiting valences of $+1$, $+5$, and $+7$. A remarkable feature of these substances is their ability to oxidize and reduce themselves.

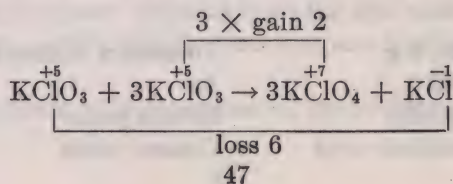
Thus if chlorine gas is passed into a cold, dilute solution of potassium hydroxide, the resulting products are potassium chloride and potassium hypochlorite. In this reaction, one atom of the molecule of free chlorine is reduced, whereas the other is oxidized; *viz.*,



If now this solution is heated, or if chlorine is passed into a warm, concentrated solution of potassium hydroxide, the final products are potassium chloride and potassium chlorate. Here again we have both oxidation and reduction of the chlorine atom taking place. Without a doubt KClO_2 is formed as an intermediate product but being unstable decomposes, so that the final equation becomes



When potassium chlorate in the crystalline state is heated strongly, we have two reactions taking place. The first one is simple decomposition, yielding oxygen; the second, oxidation of some of the chlorate to perchlorate. This second reaction may be represented by the equation



It is apparent, then, that by adjusting temperature and concentration it is possible to prepare compounds of chlorine of various valences. The reaction of chlorine with solutions of bases yields usually a maximum valence of 5. Special conditions are necessary for the production of compounds in any quantity in which the chlorine is in the heptavalent state.

EXPERIMENTAL

In the experiments to follow we shall prepare *potassium chlorate* and *hypochlorite*. Chlorine is to be passed into a solution of potassium and sodium hydroxides, thus reducing the quantity of the potassium hydroxide required.

PART A. POTASSIUM CHLORATE

Calculate the volume of chlorine required to react with 36 g. of potassium hydroxide to give the chlorate, and then calculate the weight of manganese dioxide, and the volume of concentrated hydrochloric acid (specific gravity 1.2, 40 per cent HCl) required to produce this volume of chlorine.

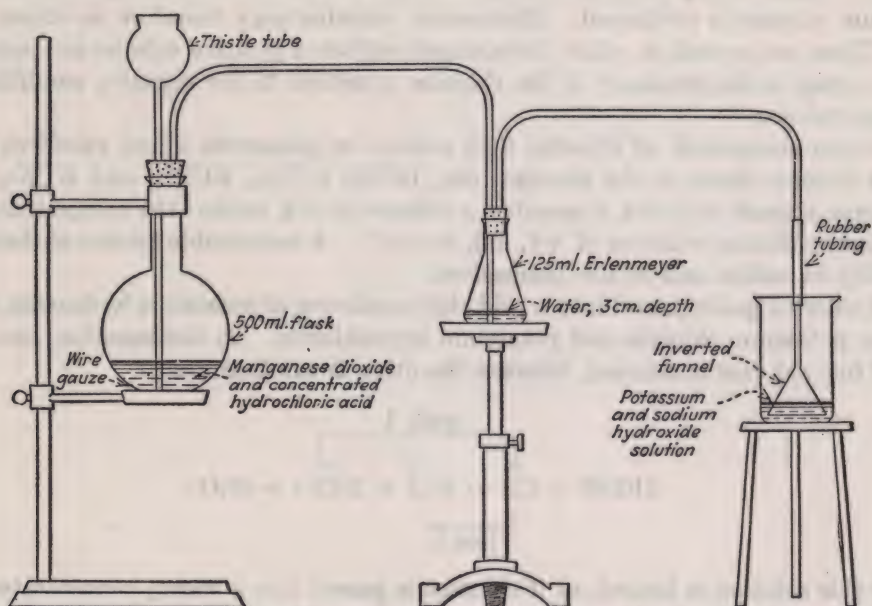


Fig. 14.—Preparation of potassium chlorate.

Apparatus :

- 500-ml. flask with two-hole stopper
- Thistle funnel
- 125-ml. Erlenmeyer flask with two-hole stopper
- 250-ml. beaker
- Funnel
- Connecting tubing
- Suction filter
- 50-ml. graduate
- Thermometer

Materials :

- | | |
|--------------------------------|--------------------|
| Potassium hydroxide, 6 g. | Potassium chlorate |
| Sodium hydroxide, 22 g. | Ice |
| Crude manganese dioxide | Litmus paper |
| Concentrated hydrochloric acid | Colored cloth |

Procedure.—Weigh out on a dish, using the rough balances, the above weights of potassium and sodium hydroxides. Dissolve these together in 45 ml. of water contained in a beaker. Withdraw 5 ml. of this solution and reserve it for Part B of this experiment, after diluting it to 20 ml. with water. The remaining 40 ml. are transferred to a 250-ml. beaker (or larger, depending on the size of funnel used) and placed under the funnel as indicated in the diagram (Fig. 14). Into the generator introduce approximately one-half more than the calculated weight of manganese dioxide. The small Erlenmeyer is used as a trap for any hydrogen chloride that passes over from the generator. A layer of water (about 3 cm. depth) is contained in this flask, and care must be taken to see that the mouth of the delivery tube extends well below the surface.

Note.—Chlorine attacks the mucous membranes seriously when inhaled, so always work under the hood.

Pour through the thistle tube one-half more concentrated hydrochloric acid than you calculated as being necessary, and allow the chlorine gas to pass through the wash bottle into the hydroxide solution. If necessary, warm the generator, in order to maintain a steady flow of gas, bubbling it rapidly through the solution until it no longer reacts alkaline to litmus paper. The heat of the reaction should be sufficient to maintain a high temperature in the solution, but if it falls below 70°C. at any time heat the solution carefully.

When the solution is thoroughly saturated with chlorine, remove the beaker and funnel, scraping any crystals from the funnel into the beaker. Heat to boiling and, while still at this temperature, pour on to a suction filter. Crystallization should begin immediately, while the solution is still in the filter. As soon as the last of the liquid has been drawn through the filter, disconnect the suction pump (remove the connecting tube), add 10 ml. of water to the filtrate, transfer to the beaker once more, and again heat to boiling. The solution is now poured over the crystals already existing in the filter, allowed to stand a few moments without suction, and then filtered dry, using the suction pump. In this way all the potassium chlorate is washed through into the filtrate. Transfer the filtrate as quickly as possible to a beaker, where it is cooled to 0°C. Crystals of the chlorate should appear during the cooling; but if there is no sign of crystallization, gently evaporate the solution to about two-thirds of its original volume, and treat as above.

Using a common filter, filter out the crystals and wash with a few cubic centimeters of cold water. They are then dried and weighed. Test the filtrate with a few drops of silver nitrate solution and explain the result.

PART B. POTASSIUM HYPOCHLORITE

The dilute solution of the hydroxides of sodium and potassium, prepared in Part A, and reserved in a test tube, is taken and placed in an ice bath or in a bath of running water. Chlorine from the generator is passed into this solution for a few minutes. Remove the test tube and acidify the solution with a little dilute hydrochloric acid. Test the bleaching properties of the resulting solution using

- a. Litmus paper
- b. Ink on filter paper
- c. Colored cloth

Record your observations.

EXPERIMENTS

Obtain a few crystals of potassium chlorate from the side shelf.

1. Dissolve a few in water, acidify slightly, and compare the bleaching action with that of the solution above.

2. Heat a few of the crystals with concentrated hydrochloric acid. Describe the reaction and write an equation.

TREATMENT OF DATA

Calculate the percentage yield of potassium chlorate on the basis of the potassium hydroxide used.

EXERCISES

1. From the following data, draw solubility curves for KClO_3 , NaCl , KCl , and NaClO_3 :

Solution	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
KClO_3	3.3	5.0	7.1	9.1	14.5	19.7	26.9	32.5	39.6	47.5	56.0
NaCl	35.6	35.7	35.8	36.0	36.3	36.7	37.1	37.5	38.0	38.5	39.1
KCl	28.5	31.2	34.3	37.3	40.1	43.9	45.5	48.3	51.0	53.8	56.6
NaClO_3	82.0	89.0	99.0	123.5	147.0	175.0	204.0

Data given are for the number of grams of substance that will dissolve in 100 g. of water at the temperature indicated.

2. Show from the curves why the products in A should be potassium chlorate and sodium chloride rather than sodium chlorate and potassium chloride.

3. Why does potassium chlorate stay in the filtrate at boiling temperatures, whereas it is the sodium chloride that does so at room temperature?

4. How is "bleaching powder" prepared? How does it react with an acid? Write equations.

5. Write equations to show *two* methods of preparation of potassium bromate.

ASSIGNMENT 12

CATALYSIS. SYNTHESIS OF SULFUR TRIOXIDE AND SULFURIC ACID

In the preparation of copper sulfate (Assignment 8) the copper was oxidized from its elementary condition to its highest valence state by simply dissolving it in nitric acid.

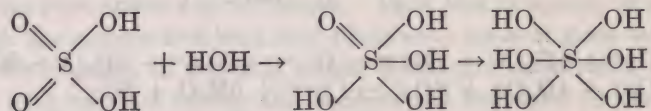
A great many reactions, however, can be brought about only if another, apparently inactive, substance is also present. When we have such a substance which, while not apparently entering into the reaction itself, hastens the reaction, or permits of its taking place, without being used up during the process itself, we designate that substance as a *catalyst*.

When sulfur is ignited in oxygen, the product of combustion is SO_2 , a compound in which the sulfur atom exhibits a valence of +4. The maximum valence of sulfur is +6 as evidenced by the compounds SO_3 and H_2SO_4 . The reaction involving the oxidation of the sulfur atom from +4 to +6 is of extreme importance, since it forms the basis of the manufacture of one of our most important commercial chemicals, *viz.*, sulfuric acid.

Importance of Sulfuric Acid.—Sulfuric acid ranks perhaps second only to water in importance as a chemical compound, owing no doubt to the fact that it exhibits various properties according to its concentration. In the diluted state it is highly ionized, and consequently it is a very strong acid, while in the concentrated condition it is also a powerful oxidizing agent as well as being an excellent dehydrating agent.

1. *As an Acid.*—Sulfuric acid exhibits all of the properties common to acids and, being a strong acid, forms stable salts with the metals.

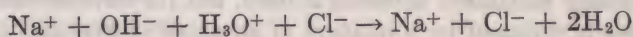
2. *As a Dehydrating Agent.*—When water is added to concentrated sulfuric acid, a large amount of heat is liberated, and a shrinkage in total volume results. (*It is extremely dangerous to add water to the concentrated acid owing to the formation of steam within the acid with subsequent spattering of the liquid. Hence when it is necessary to dilute sulfuric acid, the acid must be added slowly to the water.*) The water is absorbed into the sulfuric acid possibly according to the equations:



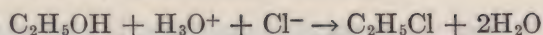
The affinity of sulfuric acid for water does not apply only to those cases where water is present as such, but sulfuric acid is also capable of removing the elements hydrogen and oxygen from compounds in such proportions as would form the water molecule H_2O . It is this reaction that makes the acid such an important reagent in the preparation of a great many organic compounds.

Whereas reactions between inorganic substances take place in solution quite smoothly and readily owing to the existence of the reactants in the ionic condition, most organic reactions take place very slowly and in many cases incompletely, since they are but slightly, if at all, ionized. Thus although we might consider the alcohols organic bases, their reactions with highly ionized acids are very slow as compared to those with inorganic bases.

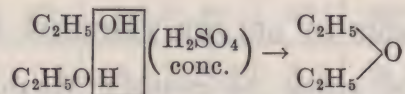
Since we believe that neutralization consists of the interaction between H_3O^+ ions and OH^- ions, and in the cases of inorganic acids and bases these ions are present in the solutions as such, it is not difficult to understand why such reactions take place rapidly. Thus



takes place rapidly and completely; but

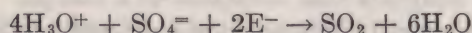


proceeds very slowly. In the presence of concentrated sulfuric acid, however, a great many reactions that would be difficult to obtain otherwise, take place readily, the acid removing H and OH to form the water molecule, thus leaving the remaining radicals free to combine; *e.g.*, manufacture of ether:

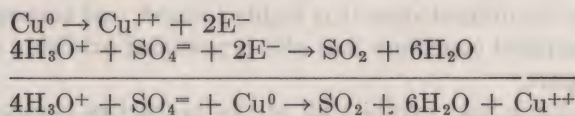


Other examples are cited in Assignment 13.

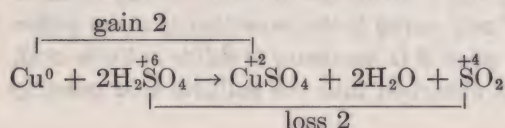
3. *As an Oxidizing Agent.*—In dilute sulfuric acid, the S^{+6} is in the $\text{SO}_4^{=}$ ion and is quite stable. In the concentrated acid the molecule appears to have a tendency to decompose whenever possible to allow the sulfur to attain the valence state of +4.



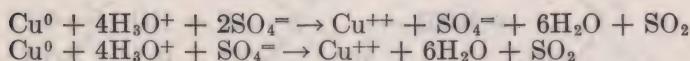
Thus, provided there is a reducing agent present capable of supplying these electrons (gaining positive valence), a reaction may take place. It is for this reason that metals such as copper and bismuth, which appear below H_2 in the electromotive series and are thus too mild as reducing agents to displace the hydrogen from dilute acids, react quite vigorously with concentrated sulfuric acid. In this case it will be noted that it is the sulfur atom and not the hydrogen which is reduced.



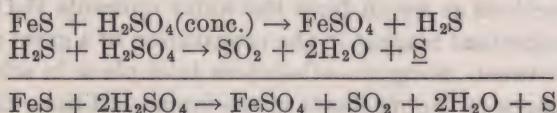
For the student not accustomed to writing "ionic equations" the reaction may be written according to the *valence change* method:



or



As in the cases of other oxidizing agents, we shall not have any reducing agents liberated in the presence of concentrated sulfuric acid. H_2 , H_2S , HI , etc., could not therefore be obtained by double-decomposition reactions involving the use of this acid; *e.g.*,



EXPERIMENTAL

Formerly all sulfuric acid was made by the "lead-chamber" process, which consisted primarily of the oxidation of sulfur dioxide in the presence of steam, by oxides of nitrogen.

This method is now supplemented by the "contact process," a catalytic method, which depends on the fact that SO_2 may be oxidized to SO_3 by molecular oxygen in the presence of certain catalysts. Usually platinized asbestos is used, but for obvious reasons in the experiment to follow this substance is replaced by a mixture of an oxide of iron and asbestos.

Apparatus:

3-in. funnel
Calcium chloride tube
Combustion tube about 8 in. long
Suction flask and pump
Test tube with two-hole rubber stopper
Connecting tubes and stoppers

Materials:

Sulfur, 5 g.	Potassium chlorate
Mixture of ferric oxide and asbestos	Sugar
Calcium chloride	Pieces of zinc
Glass wool	
Granular pumice	

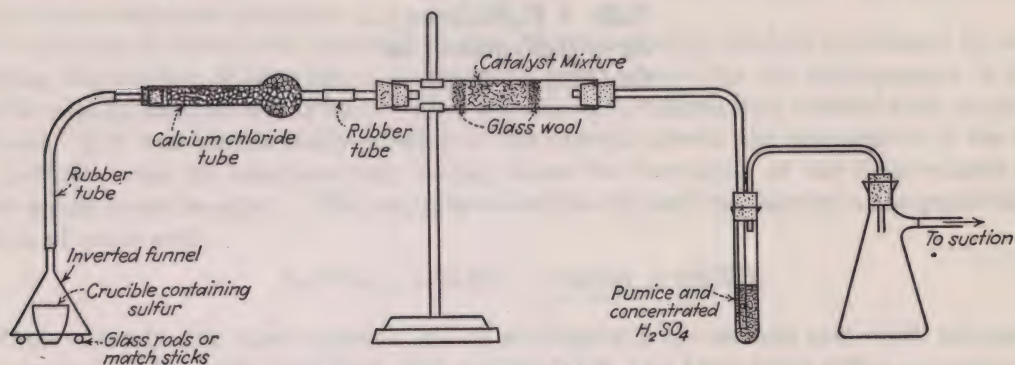


FIG. 15.—Preparation of sulfuric acid.

Procedure.—Arrange an apparatus such as is indicated in the diagram (Fig. 15). Place approximately 5 g. of sulfur in a crucible and weigh the crucible and contents to the nearest 0.1 g. The funnel is supported on match sticks or small glass tubing to allow of free access of air to the sulfur. The drying tube is filled loosely with calcium chloride, held in place by loose wads of glass wool. Introduce into the combustion tube enough of the oxide-asbestos mixture to form a section in the center of the tube about 2 in. in length. Pack this in loosely so as not to prevent free passage of gas through the system and hold it in place with wads of glass wool. The test tube is half-filled with granular pumice, to which is added 6 ml. of concentrated sulfuric acid. Insert the two-hole stopper with its glass tubing and connect the test tube to the suction flask but *not* to the combustion tube. Turn on the suction slowly when it will be found that the pumice rises to the top of the liquid and packs together to form a porous layer. Disconnect the test tube and weigh it with its contents to the nearest 0.1 g.

Now complete the connections and heat the combustion tube to a dull red heat. Ignite the sulfur in the crucible and adjust the suction until the sulfur fumes are all drawn through the system. Some white fumes of sulfuric acid may appear in the suction flask but these should be very faint. Maintain the temperature of the catalyst until most of the sulfur has burned, and the residue is not readily ignited. Allow the apparatus to cool, then disconnect the test tube, and weigh it with its contents. Weigh the crucible with any residue which it contains.

EXPERIMENTS

1. Add a few drops of concentrated sulfuric acid to:
 - a. A small crystal of potassium chlorate.
 - b. A few crystals of sugar.

Note the results and write equations.

2. Add 5 ml. of concentrated sulfuric acid to a small piece of zinc in a hard-glass test tube. Heat carefully, and see if you can identify the products. Compare this reaction with that of zinc with dilute sulfuric acid. Write the equations.

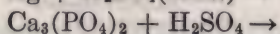
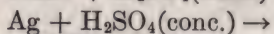
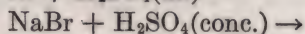
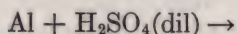
TREATMENT OF DATA

1. From the loss in weight of the crucible calculate the theoretical weight of SO_3 which should be obtained.

2. Using the gain in weight of the test tube calculate the percentage yield in the process.

EXERCISES

1. What would be the effect on your yield of heating the catalyst too highly? Explain.
2. Why is it necessary to absorb the SO_3 in concentrated H_2SO_4 ?
3. Complete and balance the following equations:

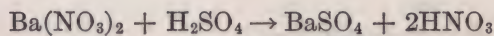


ASSIGNMENT 13

PREPARATION OF ACIDS FROM SALTS. NITRIC ACID

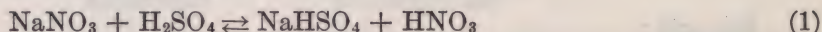
For the preparation of pure inorganic compounds, several methods are used depending upon the substance under consideration. These reactions are those which will favor the displacement of the equilibrium in the direction of the formation of maximum yield of the substance desired. In general, the formation of a gas, a precipitate, or little-ionized molecule or complex ion favors complete reaction, so that it is customary to use reagents that bring about the formation of one of the above-mentioned products.

In the case of nitric acid, although most of the present-day product is obtained by methods involving the fixation of nitrogen, a great deal is still prepared by the displacement of the acid from its salts by another strong acid. Thus if a nitrate is treated with sulfuric acid, nitric acid is liberated. If it was commercially possible to use barium nitrate, the preparation of the acid by this method would be comparatively simple, since the formation of the little-soluble barium sulfate would favor reaction. The precipitate could be filtered out, leaving a comparatively pure solution of nitric acid.



Unfortunately, the most common salt of nitric acid is the sodium salt, Chili saltpeter, and as there are but few salts of sodium that are insoluble, and their acids either expensive or too weak to bring about displacement of the stronger acid HNO_3 , we are compelled to adjust conditions so that we may displace equilibrium by other means.

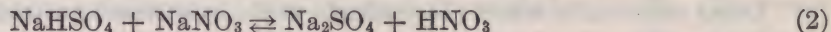
If sodium nitrate is treated with concentrated sulfuric acid, since both sulfuric and nitric are strong acids, a reversible reaction is set up.



At equilibrium, then, we have a mixture of four substances. On comparing the boiling points of the two acids, however, we find that, although both are volatile at elevated temperatures, the transition point for sulfuric acid at atmospheric pressure is $250^\circ\text{C}.$, whereas that of nitric acid is about $90^\circ\text{C}.$ Consequently if a mixture at equilibrium, such as represented by the equation above, is heated to temperatures between the boiling points of the two acids, the nitric acid volatilizes before the sulfuric acid does, and we can draw the reaction to apparent completion as a result of the formation of this volatile product.

If the hydrogen salt which remains is heated with an excess of sodium nitrate to higher temperatures, it is possible to replace the other hydrogen atom and liberate another molecule of nitric acid.

The latter process is followed in some of the commercial processes involving the above reaction but yields a less pure acid owing to decomposition at these higher temperatures. In the laboratory it is customary to stop the reaction at the formation of the primary salt.



Object of the Experiment.—The following experiments and exercises are designed to acquaint us with the preparation of a compound involving a double-decomposition reaction, and also as an introduction to the important field of chemical equilibrium with which we shall deal in more detail at a later stage. In addition, since nitric acid is one of our most important chemicals,

ranking with sulfuric and hydrochloric, we have an opportunity in the following experiments to study the reasons for the importance of this acid in the commercial field.

Reactions of Nitric Acid.—Nitric acid owes its wide use in industry to three types of reactions into which it may enter.

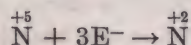
1. *It Is a Strong Acid.*—By this we understand that it is completely ionized in dilute solutions and consequently we find it evidencing all of the reactions peculiar to acids, such as neutralization.

2. *It Is a Powerful Oxidizing Agent.*—As contrasted with sulfuric acid which is an oxidizing agent only when concentrated, nitric acid is a powerful oxidizing agent in both dilute and concentrated solutions. This is due to the tendency of the nitrogen atom to return to a lower valence state than that in which it exists in nitric acid. Like chlorine and sulfur, nitrogen exhibits a number of valences, ranging from +5 to -3, intermediate valences being +4, +3, +2, +1, and 0.

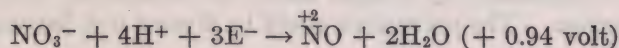
In nitric acid, then, the nitrogen atom exhibits its highest valence and in the presence of even extremely weak reducing agents, such as metallic copper, we have reduction of the nitrogen taking place. The more active the reducing agent, the greater the extent of this reduction, as we shall see during the course of the experiments to follow.

The more common reactions of nitric acid may be represented by the skeleton equations listed below.

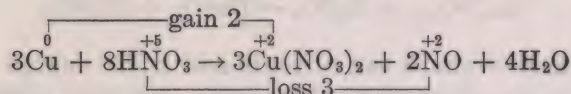
a. Dilute acid:



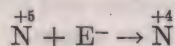
or ionically



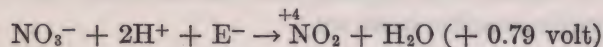
Example:



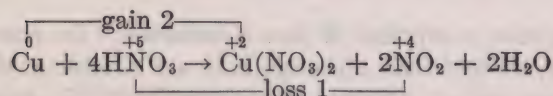
b. Concentrated acid:



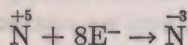
or ionically



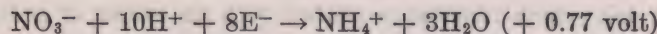
Example:



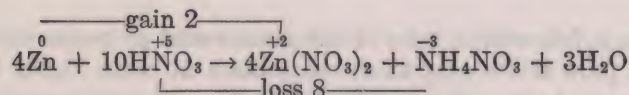
c. Both acids with powerful reducing agents:



ionic equation,

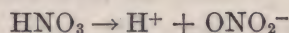


Example:



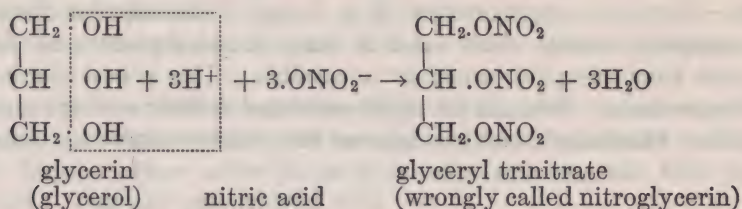
Other reactions in which the products would be molecular nitrogen or lower oxides of nitrogen are also possible. In the above equations the symbol E^- represents an electron, while the losses and gains refer to positive valence. It is to be understood that the proton (H^+) exists in solution in the hydrated form H_3O^+ , the *hydronium* ion. The ionic equations are expressed with the oxidation-reduction potentials of the reactions. The interested student is referred to the Appendix for an explanation of these.

3. *It Is a Nitrating Agent.*—With organic compounds nitric acid may react in two ways, depending upon the substance being attacked. Since, for the most part, organic substances are little ionized, reactions do not take place so smoothly as in the case of inorganic compounds. In the presence of dehydrating agents we may obtain reactions corresponding to neutralization in which the nitric acid acts as a normal acid; *viz.*,

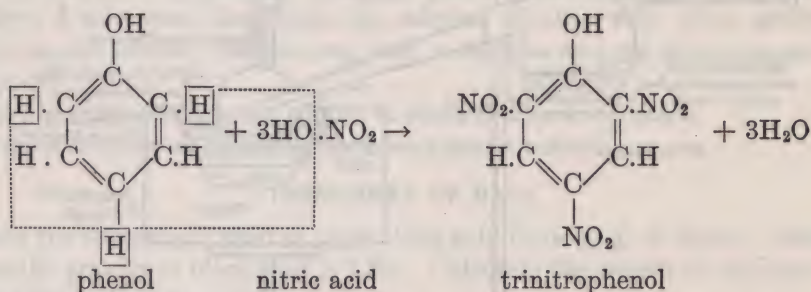


On the other hand, it may react in such a manner as to lose an OH group according to the structural formula $\text{OH}.\text{NO}_2$ for nitric acid.

Thus if glycerol is treated with concentrated nitric acid in the presence of concentrated sulfuric acid, we have a reaction taking place corresponding to the inorganic reaction between acids and bases.



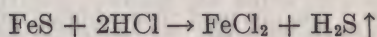
With substances like phenol (carbolic acid), we have the hydrogen removed from the organic compound and the hydroxyl group from the nitric acid when these two substances are brought together in the presence of concentrated sulfuric acid. The resulting product is *nitrophenol* or *picric acid*.



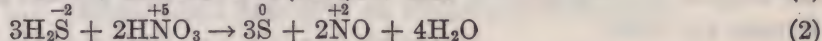
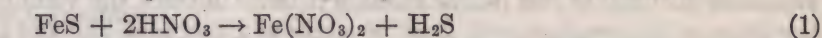
This type of reaction is of great importance in the industrial field. From the above examples see if you can differentiate between organic nitrates and nitro- compounds.

It is obvious that, when nitric acid is used as an acid, the possibility of these secondary reactions must be taken into consideration. For example, we cannot expect to obtain only hydrogen by reacting upon nitric acid with a metal, even though that metal be above hydrogen in the electromotive series. Similarly, it is unlikely that any reducing agent will be liberated as a final reaction product in the presence of this acid whether it be dilute or concentrated.

Thus, although



with nitric acid a second reaction takes place so that hydrogen sulfide is not obtained.



If the student will bear these reactions in mind, a great many mistakes will be avoided.

Caution.—Nitric acid is a powerful corrosive attacking the flesh and clothes rapidly. The fumes are poisonous, so work under a hood whenever possible.

EXPERIMENTAL

In order to save time, the student is advised to begin with Part B of this experiment, unless directed otherwise by the instructor.

PART A. PREPARATION OF NITRIC ACID

Apparatus:

125-ml. flask
250-ml. retort
Pneumatic trough
50-ml. graduate

Materials:

Concentrated sulfuric acid
Sodium nitrate, 25 g.

Concentrated nitric acid
 BaCl_2 solution

Procedure.—Introduce approximately 25 g. (rough balances) of sodium nitrate into a clean and dry glass-stoppered retort. Care must be taken to see that none of the salt adheres to the sides of the retort where reaction would be impossible. This is best eliminated by pouring the salt through a paper cone. Next, 30 ml. of concentrated sulfuric acid are carefully added through a glass funnel, after which the retort is stoppered and its stem introduced into the neck of a small

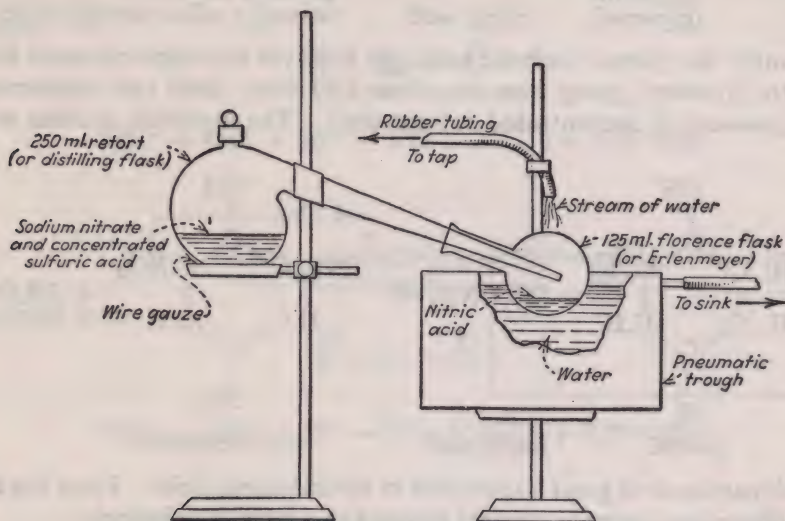


FIG. 16—Preparation of nitric acid.

flask as indicated in the diagram (Fig. 16). This, in turn, is supported in a pneumatic trough, the outlet of which is so arranged as to permit drainage into the sink. Connect a rubber tube to the tap and fasten so as to have a small stream of water constantly playing over the flask. A wire gauze is placed under the retort and the temperature gradually raised by means of a burner until the nitric acid begins to distill over. Do not heat to too high a temperature. When about 10 ml. of distillate have been collected, and brown fumes begin to appear in the retort, remove the flask and *allow the retort to cool* before washing it out. Record the volume of your product. Dilute a few drops of the product with 2 ml. of water in a test tube and add a few drops of BaCl_2 solution. Explain the result.

PART B. EXPERIMENTS WITH NITRIC ACID

Materials:

Concentrated nitric acid
Absorbent cotton, 4 g.
Concentrated sulfuric acid
Dilute hydrochloric acid

Dilute sodium hydroxide
Pieces of zinc and copper
Litmus paper

1. Preparation of Guncotton.

Introduce 30 ml. of concentrated nitric acid into a clean, dry beaker. Place the beaker and contents into a vessel containing water in order to keep the solution cool, and then cautiously add 40 ml. of concentrated sulfuric acid to the nitric acid with constant stirring. Allow mixture to cool and while still in the water bath add, *shred by shred*, 2 g. of cotton, pressing down firmly each portion of the cotton as added, with a glass rod. When all of the cotton has been added, cover the beaker with a watch glass and transfer it and the water bath to the hood where it is left for 15 min. At the end of this period lift the cotton out of the acid mixture, using the glass rod, and drop it into a large beaker of water. Rinse it thoroughly and then *wash until there is no reaction when blue litmus is pressed against it*. Squeeze out as much water as possible and then press the product between filter papers, after which *the guncotton is shredded as finely as possible and allowed to dry thoroughly*.

(Warning.—Never leave this product in your desk nor throw into the waste jars. It must be burned.)

When dry, place on a piece of asbestos or other fireproof material, and place a similar amount of untreated cotton close by. Ignite both portions and compare the rates of combustion.

2. *Reactions with Metals*.—Place a few pieces of metallic zinc in a test tube and cover with dilute hydrochloric acid. Test any gas evolved with

a. A flame.

b. Moist litmus paper.

Now place a similar amount of zinc in another test tube and add 20 ml. of water and 2 ml. of the nitric acid you have prepared. Test any gas evolved as above. Allow the reaction to proceed for about 5 min. and then make the solution alkaline with dilute sodium hydroxide. Warm the mixture and test any gas evolved with moist blue and red litmus papers. *Cautiously* smell the vapor.

Repeat the above reactions using copper in place of zinc in all cases.

Write the equations for all reactions that have taken place.

TREATMENT OF DATA

1. Calculate the theoretical yield of pure nitric acid from 25 g. of sodium nitrate.
2. The specific gravity of nitric acid is 1.52. Calculate the weight of acid you obtained and the percentage yield in the process.

EXERCISES

1. What color is pure nitric acid? How do you account for the color of the acid you prepared? Write an equation.
2. Could hydrochloric acid be used in the preparation in place of sulfuric acid? Give reasons for your answer.
3. Pure cotton is composed of cellulose, a complicated compound whose molecules may be represented by the formula $(C_6H_{10}O_5)_y$ where the value of y is unknown. Assuming a simplified formula $(C_6H_{10}O_5)_2$, write an equation for the formation of guncotton using the following information:
 - a. Guncotton is cellulose *hexanitrate*.
 - b. Cellulose behaves in this reaction like a base with six replaceable OH groups.
4. Explain the function of the sulfuric acid in the above process.
5. List *five* commercial products that are the result of the action of nitric acid on organic compounds.

The first part of the book is devoted to a general survey of the history of the subject. It begins with a discussion of the early attempts to explain the phenomena of the subject, and then proceeds to a more detailed examination of the various theories which have been advanced. The author's own views are presented in a clear and concise manner, and are supported by a wealth of references to the original sources. The second part of the book is devoted to a more detailed examination of the various theories which have been advanced. The author's own views are presented in a clear and concise manner, and are supported by a wealth of references to the original sources.

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ASSIGNMENT 14

PREPARATION OF ACIDS FROM SALTS. ACETIC ACID. FRACTIONAL DISTILLATION

In the preparation of nitric acid from a nitrate (Assignment 13) we have seen that it is necessary to adjust the conditions so that the equilibrium is displaced in the desired direction, and this was done by making use of concentrated sulfuric acid and heating the reaction mixture so that the lower-boiling nitric acid distilled off.

When we are preparing a weak acid like acetic acid ($K = 1.8 \times 10^{-5}$), we find that by using any strong acid with the salt the equilibrium is already displaced well in the direction of a complete reaction, as shown by the expression



The reverse reaction can proceed only to an extremely small extent, owing to the feeble ionization of acetic acid. This is an example of a reaction that approaches completion because of the formation of a slightly ionized product. It is therefore not necessary in this case to take special precautions to secure a complete reaction, and we are faced only with the problem of separating the desired reaction product in a pure state.

Acetic acid is prepared on the industrial scale by the destructive distillation of wood. When wood is heated out of contact with the air, water vapor is at first given off; but when a temperature of about 160°C . is reached, there distills over an acidic distillate which is known as "pyroligneous acid." At higher temperatures much gas and tar are obtained leaving behind charcoal and some ash. The pyroligneous acid contains many important products, the chief ones being methyl alcohol, acetic acid, and acetone. This mixture is neutralized with "milk of lime" (slaked lime), forming calcium acetate which can be readily separated from the other products. Pure acetic acid is obtained by treating this salt with sulfuric or hydrochloric acid and distilling.

A dilute solution of acetic acid, containing other substances, may be prepared by allowing dilute alcohol to oxidize in the air under the influence of certain bacteria. The product is known as *vinegar*.

Acetic acid is at the present time produced synthetically on a large scale from acetylene, C_2H_2 , by a special catalytic process.

The pure acid is a solid below 16.7°C . and has much the appearance of ice. Hence the name *glacial acetic acid*. However, the acid absorbs water very readily, and under ordinary conditions of preparation we obtain a solution of acetic acid in water. If glacial acetic acid is desired, it is necessary to fuse the acetate first, and then distill with concentrated sulfuric acid, special precautions being taken to prevent the distillate from absorbing water.

EXPERIMENTAL

Acetic acid is to be prepared in this experiment by the reaction between calcium acetate and concentrated hydrochloric acid.

In this reaction the acetic acid formed is mixed with water and calcium chloride. Since pure acetic acid boils at 118°C ., the acid can be distilled off from the non-volatile salt. Water vapor will also come off, however, and the receiver will thus contain a solution of acetic acid in water. The problem of separating two mutually soluble liquids from one another is solved by the application of *fractional distillation* or *rectification*.

This process can be understood by considering its application to the case of separating water and acetic acid. Since water boils at $100^{\circ}\text{C}.$, the vapor coming from the boiling solution will at first consist largely of water vapor. There will also be present, however, some acetic acid vapor, and the proportion of this will increase as the boiling continues and water is removed from the solution, the boiling point likewise rising. It is not possible in one distillation therefore to separate the two liquids completely. If, however, the distillate is collected in separate fractions, corresponding to the liquid first condensing, later a portion, etc., it is obvious that the first fractions will consist largely of water, later fractions considerable amounts of both water and acid, while the last fraction will be largely acetic acid.

These separate distillates are now distilled over again with further separation into fractions. Eventually, if the process is repeated a number of times, there will be obtained at one end of the series nearly pure water, and at the other nearly pure acetic acid.

Industrially, and in advanced laboratory work, this process of fractional distillation is carried on in a continuous series by use of apparatus which makes it possible to proceed with the successive distillations in rapid sequence. When used in this manner, the process is usually called rectification and the apparatus used is known as a *rectifying column*.

In the present experiment the fractional distillation is to be carried out only during its initial stages, so that the product obtained will not be pure acetic acid but will contain a high percentage of the acid.

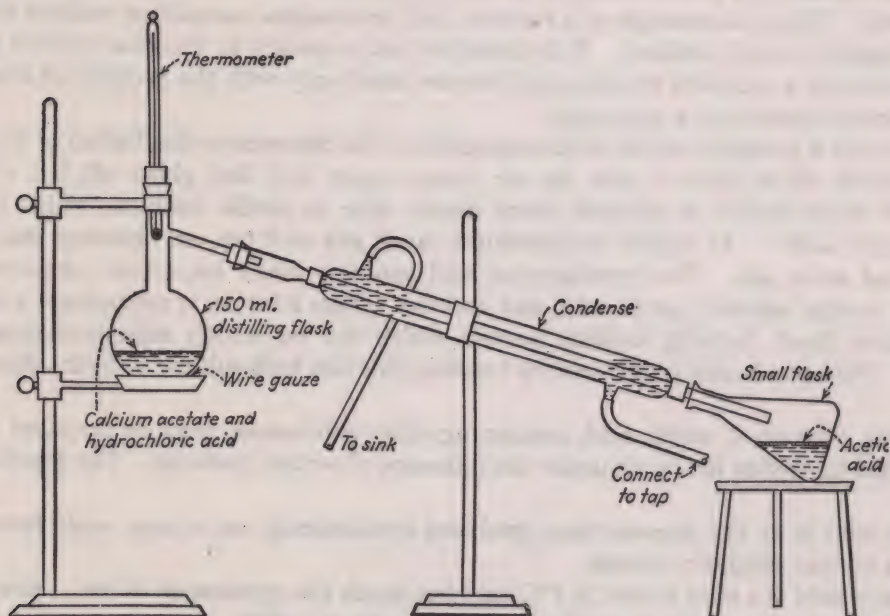


FIG. 17.—Preparation of acetic acid.

Apparatus:

150-ml. distilling flask
Condenser
125-ml. Erlenmeyer flask

50-ml. graduate
Thermometer

Materials:

Calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, 20 g.
Concentrated hydrochloric acid
Concentrated sulfuric acid
Pieces of zinc
Alcohol

Procedure.—Set up the distillation apparatus as shown in the diagram (Fig. 17). Weigh out the calcium acetate on the rough balances, and place it in the distilling flask. Add 17 ml. of concentrated hydrochloric acid, being careful to prevent any acid from running down the side arm of the distilling flask. Shake the mixture a little and let it stand for a few minutes before heating. Turn a slow stream of water through the condenser and heat the reaction mixture carefully until the liquid begins to distill over. Keep the temperature in the flask below 120°C . and continue the distillation until the temperature commences to rise rapidly or until the liquid in the distilling flask is nearly all gone.

Allow the distilling flask to cool, clean it, and then place the distillate in it. Wash out the condenser and reconnect the apparatus. Redistill, discarding any distillate coming over at temperatures below 110°C . Collect that portion distilling between 110 and 118°C . This is your final product. Measure its volume.

EXPERIMENTS

1. Test a few cubic centimeters of your product with silver nitrate solution and explain the result.
2. Dilute about 5 ml. of your product with an equal volume of water and add a small piece of zinc. Compare the reaction with that of dilute hydrochloric acid and zinc. Write the equation.
3. To 5 ml. of acetic acid add 5 ml. of alcohol (methyl or ethyl) and 5 ml. of *concentrated* sulfuric acid. Heat the mixture and notice the odor. Write the equation for the reaction. What is the function of the sulfuric acid? Compare this reaction with that between acetic acid and sodium hydroxide.

TREATMENT OF DATA

1. Assuming your product to be nearly pure acetic acid, calculate its weight, taking the specific gravity of acetic acid as 1.06.
2. Calculate the percentage yield in your preparation, based on the weight of calcium acetate used.

EXERCISES

1. Why can hydrochloric acid be used in this preparation, but not in the preparation of nitric acid?
2. What is the product left in the distilling flask after the first distillation? What effect does it have on the boiling point of the liquid?
3. Why does most of the acetic acid distill over at a temperature below the boiling point of pure acetic acid?

The first part of the report deals with the general situation of the country. It is a very interesting and well-written account of the country and its people. The author has done a great deal of research and has gathered a wealth of material. The second part of the report deals with the political situation. It is a very interesting and well-written account of the political situation and the various parties and movements. The third part of the report deals with the economic situation. It is a very interesting and well-written account of the economic situation and the various industries and trades. The fourth part of the report deals with the social situation. It is a very interesting and well-written account of the social situation and the various classes and groups. The fifth part of the report deals with the military situation. It is a very interesting and well-written account of the military situation and the various armies and navies. The sixth part of the report deals with the cultural situation. It is a very interesting and well-written account of the cultural situation and the various arts and sciences. The seventh part of the report deals with the religious situation. It is a very interesting and well-written account of the religious situation and the various religions and sects. The eighth part of the report deals with the legal situation. It is a very interesting and well-written account of the legal situation and the various laws and courts. The ninth part of the report deals with the administrative situation. It is a very interesting and well-written account of the administrative situation and the various departments and agencies. The tenth part of the report deals with the foreign relations situation. It is a very interesting and well-written account of the foreign relations situation and the various treaties and agreements.

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ASSIGNMENT 15

HIGH-TEMPERATURE REACTIONS. PREPARATION OF POTASSIUM PERMANGANATE

We have already discussed under the heading Oxygen Compounds of Chlorine an element that occurs in Group VII of the periodic system. Related to the halogen group we have another group which shows a definite resemblance to the halogen family, although evidencing a more metallic nature than we meet with in the former case.

As regards valence states, we find the same valences exhibited in both groups with this exception (which is apparent when we consider the nature of the atom), that whereas chlorine, being a typical non-metal, forms its most stable compounds with metals, itself assuming negative valence, manganese being metallic in character tends to attain positive valence. Thus, although the maximum valence possible should be +7, and the minimum valence -1, we never meet with compounds of manganese in which the element is in this latter valence state.

The valences usually exhibited are 0, +2, +3, +4, +6, and +7, but, just as in the case of chlorine the atom seemed to avoid certain valence states, manganese also appears to form very unstable compounds when it assumes valences of +3 or +4, unless they are slightly soluble substances as in the case of manganese dioxide. The most important salts met with, therefore, correspond to valence states of +2, +6, and +7.

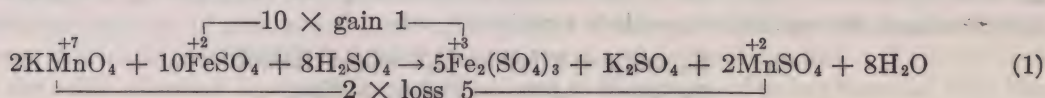
We learn when considering valence that, if an element is capable of assuming more than one valence state, the higher the valence, the more acidic will be the oxide. In the case of manganese (as in the case of chromium, later), we have an example of an element that may be either non-metallic or metallic, according to its valence state. Consequently, if we consider the different oxides, we shall find a gradual increase in acidity as valence increases. A table of the oxides and salts corresponding to these valence states is given below.

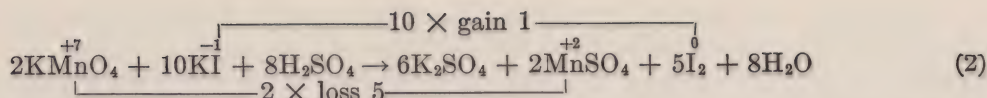
Oxide	Salt	Acid
MnO, basic.....	MnCl ₂ , stable to water	None
MnO ₂ , amphoteric.....	MnCl ₄ , hydrolyzed and unstable	$\left. \begin{array}{l} \text{H}_2\text{MnO}_3 \\ \text{Mn}(\text{OH})_4 \end{array} \right\} \text{amphoteric}$
MnO ₃ , acidic.....	No chloride	H ₂ MnO ₄ , weak acid
Mn ₂ O ₇ , acidic.....	No chloride	HMnO ₄ , strong acid

Thus the stable bivalent states are those in combinations with non-metals or acid radicals, such as the compounds MnCl₂ and MnSO₄, whereas we find the higher valences exhibited exclusively in acid radicals (where the element is definitely a part of the radical itself) as in the compounds K₂⁺⁶MnO₄ and KMnO₄⁺⁷.

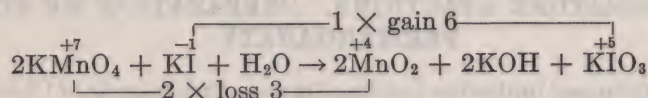
The natural tendency in the presence of a reducing agent is therefore to revert to a lower, *i.e.*, more basic, valence state. We must be careful, however, to differentiate between reduction in an acid solution and reduction in alkaline or neutral media.

Permanganates as Oxidizing Agents. 1. *In an Acid Solution.*—In acid solutions we have reversion to the bivalent state, *e.g.*,

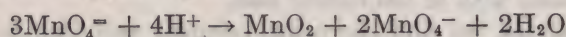




2. *In Basic or Neutral Solutions.*—In such solutions we have reversion to the tetravalent state. This type of reaction is no doubt due to the very low solubility of the hydrated manganese dioxide which precipitates out as fast as it is formed. In an acid solution this would be soluble and so the reaction may proceed until the bivalent state is reached.



The manganese compounds, in which the valence number of the manganese is +6, decompose when their solutions are acidified, yielding the dioxide and *permanganate* according to the equation,

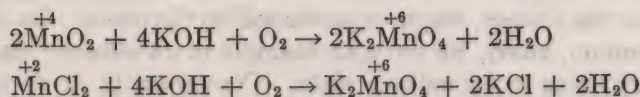


EXPERIMENTAL

Since manganese dioxide, MnO_2 , is only slightly soluble, we would expect to find it occurring in nature, and we meet with it under the name of "pyrolusite" as the most common source of manganese. In the presence of acids this compound is a good oxidizing agent, as we would expect, knowing the tendency of manganese to revert to a valence of +2 in an acid solution. At the same time, powerful oxidizing agents should be capable of oxidizing the manganese in this compound to a higher valence state.

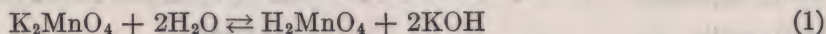
If oxidation is carried out in alkaline media, the valence number +6 is assumed; *i.e.*, *manganates* are obtained.

Examples:

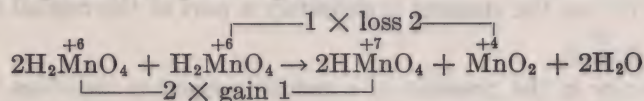


Solutions of these salts are dark green in color and are stable only when concentrated or in the presence of excess of base. If the dark-green solution of the manganate in a little water is poured into a large volume of water, a purple solution of *permanganate* and a brown precipitate of hydrated manganese dioxide are formed.

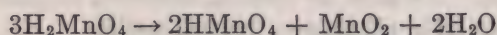
This reaction is due to the fact that K_2MnO_4 , being the salt of a weak acid, is considerably hydrolyzed in solution. An equilibrium is therefore set up as in the equation



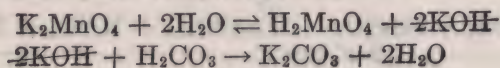
A second reaction now sets in, in which a part of the manganic acid produced is oxidized to permanganic acid, and part is reduced to manganese dioxide. We have consequently another example of self-oxidation and reduction (see also experiment on oxygen compounds of chlorine). This reaction may be represented by the equations



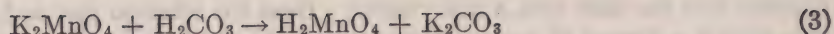
or



The reaction, however, takes place slowly in aqueous solutions; but if an acid is added, even as weak a one as H_2CO_3 , the KOH formed is removed, and consequently the equilibrium is disturbed and the reaction takes place completely, *viz.*,

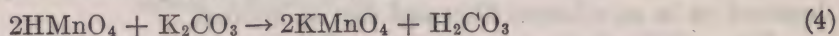


or



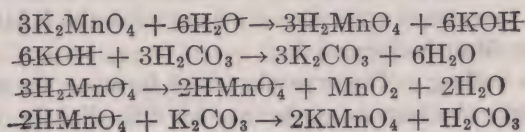
represents the total reaction.

Since H_2MnO_4 is a very weak acid, it cannot displace H_2CO_3 and consequently does not act with the K_2CO_3 . It is rapidly oxidized, however, as in Eq. (2), to permanganic acid, which being a strong acid reacts with a part of the K_2CO_3 liberating H_2CO_3 , viz.,

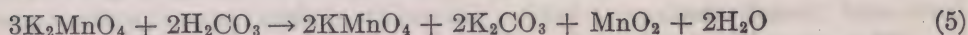


and on evaporating the solution, CO_2 is driven off and the potassium permanganate may be crystallized out.

Combining the equations representing the different reactions that take place we have,



or



Owing to the insolubility of pyrolusite (crude MnO_2), and its high melting point, in order to bring about reaction with a base it is necessary to fuse the reaction mixture. Oxygen necessary for the reaction (see equations above) is usually supplied by adding an oxygen rich salt such as KClO_3 or KNO_3 .

Apparatus:

100-ml. iron crucible	Asbestos filter and suction flask
Metal stirring rod	Porous plate
6-in. evaporating dish	Mortar and pestle
Carbon dioxide generator	

Materials:

Solid potassium hydroxide, 15 g.
Potassium chlorate or sodium chlorate, 8 g.
Pyrolusite, 15 g., or pure manganese dioxide, 10 g.
Small pieces of marble
Dilute hydrochloric acid
Sodium nitrite solution
Dilute sulfuric acid
Dilute sodium hydroxide
Hydrogen sulfide water

Caution.—Molten potassium hydroxide is a powerful corrosive causing severe burns. The charge in the crucible may scatter minute particles, so if you have goggles, wear them, if not, carry out the experiment under the hood with the glass door between your face and the crucible. Protect the hand holding the stirring rod with a glove or towel. There is no danger to the careful experimenter.

Procedure.—Grind the weighed amount of manganese dioxide in a mortar to a fine powder if it is not already in this form. Place the potassium hydroxide and the potassium chlorate in the iron crucible and heat very gently under the hood until the mixture is molten. Remove the flame and add the manganese dioxide a little at a time with stirring. When all has been added, heat the crucible and continue stirring until the mass stiffens completely. At this point, cover the crucible and heat for 10 min. at red heat. At the end of this period allow the crucible to cool and immerse it with its contents in 300 ml. of water contained in the large dish. This will disintegrate the solid, allowing the crucible to be removed. Wash any adhering material from the

crucible into the dish with a little water. Heat the solution just to boiling and at the same time pass into it a stream of carbon dioxide until the green color gives way to the purple of the permanganate. The color may be determined by touching a drop of the liquid to a piece of filter paper.

When the reaction is complete, remove the flame and allow the contents of the dish to settle. About 5 min. will be sufficient for all the sludge to settle out. The solution is now carefully decanted on to an asbestos filter and suction applied.

Note.—If the sludge is agitated and allowed to pass on to the filter before most of the liquor has been passed through, filtration will be considerably retarded.

When all of the solution has passed through the filter, the sludge is scraped from the dish onto the filter, the last traces being washed out by a stream of water from the wash bottle.

Drain the solid free of liquid and transfer the filtrate which contains the KMnO_4 to the clean evaporating dish. The residue on the filter is discarded.

Evaporate the solution by gentle boiling. The crystals which form on the sides of the dish above the solution should be rinsed into the liquid by tipping the dish slightly. When crystals begin to form on the surface of the liquid, transfer the solution and crystals to a beaker and set aside until the next day.

When crystallization has taken place, decant the remaining solution and spread the crystals to dry on a porous plate. Weigh, and record the weight of your product. Clean the brown stains from your apparatus with a few ml. of NaNO_2 solution to which is added a little dilute hydrochloric acid.

EXPERIMENTS

1. To 5 ml. of KMnO_4 add 5 ml. of dilute sulfuric acid and 10 ml. of H_2S water. Note the result and write the equation for the reaction.

2. To 2 ml. of KMnO_4 solution add 5 ml. of dilute sodium hydroxide and heat the solution until a color change takes place. Write the equation for the reaction.

TREATMENT OF DATA

1. Pyrolusite is about 80 per cent manganese dioxide. Calculate your percentage yield on the basis of the weight of pure manganese dioxide used.

EXERCISES

1. Write ionic equations to illustrate the equilibria involved in the hydrolysis of potassium manganate.

2. What would happen if the dry crystals of KMnO_4 were heated?

3. Write the formulas for manganous sulphate, calcium manganate, and aluminum permanganate.

ASSIGNMENT 16

HIGH-TEMPERATURE REACTIONS. CHROMATES AND DICHROMATES. PREPARATION OF POTASSIUM DICHROMATE

When we consider the elements occupying Group VI of the periodic system, we see that the maximum valence will be +6 and the minimum valence -2. In the case of sulfur we observed that there are intermediate valences that can be assumed, these being 0 and +4. Sulfur, being a typical non-metal, tending to exist in a negative radical or in the free state, forms very stable compounds with metals. In the case of the chromium subgroup, although it is definitely related to sulfur, the elements in this group are more metallic in character and consequently we shall not expect to find them existing in compounds in which they exhibit a negative valence.

Like manganese (Assignment 15) we can reasonably expect to find these elements, and particularly chromium, exhibiting both metallic and non-metallic tendencies, according to the valence states in which they are found. The valence states most common to chromium are +2, +3, and +6, with +3 appearing to be the valence most favored by the element. Oxides corresponding to these states are known and are listed below together with their relative basicities.

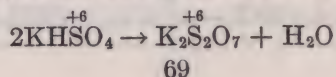
Oxide	Salt	Acid
CrO, basic.....	CrCl ₂ , stable to water	No acid
Cr ₂ O ₃ , amphoteric favoring basic.....	CrCl ₃ , partially hydrolyzed	$\left\{ \begin{array}{l} \text{Cr(OH)}_3 \\ \updownarrow \\ \text{H.CrO}_2.\text{H}_2\text{O} \\ \text{H}_2\text{CrO}_4 \\ \updownarrow \\ \text{H}_2\text{Cr}_2\text{O}_7 \end{array} \right.$
CrO ₃ , acidic.....	No chloride	

The chromous (Cr⁺⁺) compounds are blue in solution. They resemble the ferrous (Fe⁺⁺) salts closely, in that the oxide is basic only and the salts are stable to water. In the presence of air they oxidize rapidly to yield the valence +3, but much more rapidly than do the ferrous salts. They are consequently powerful reducing agents owing to this tendency of the chromium to gain positive valence (lose an electron) in order to attain the chromic condition. This valence state is more stable than the lower one, although the salts are less stable to water than are the chromous compounds. This is due to the more non-metallic nature of the trivalent chromium as evidenced by the amphoteric properties of the hydroxide.

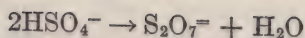
The oxide of chromium in which the element has a valence of +6 is acidic only. It is for this reason we meet with hexavalent chromium in acid radicals exclusively, *e.g.*, K₂CrO₄, BaCrO₄, Na₂Cr₂O₇, etc.

Chromates and Dichromates.—If we recall the chemistry of sulfur, we remember that we have two acid radicals in which this element exhibits a valence state of +6.

If KHSO₄ is heated strongly we have one molecule of water eliminated from two molecules of the salt, and a new compound formed. This new salt is known as the *pyrosulfate* since the valence of the sulfur has not changed and hence this must be a salt of an -ic acid.

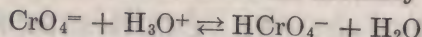


or ionically

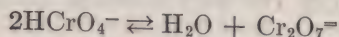


This reaction takes place only at elevated temperatures. In the case of chromium compounds having a similar valence +6, we meet with a similar reaction differing only in the ease with which the transformation takes place.

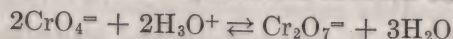
If a chromate or a dichromate is dissolved in water we have an equilibrium established between the chromate and dichromate ions without the necessity of heating; *e.g.*,



and



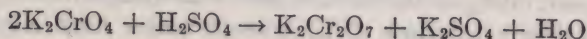
Summing, we may write the expression for equilibrium between chromate and dichromate as



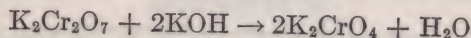
A study of this equilibrium equation reveals the fact that addition of any acid (H^+) will favor the formation of the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) whereas the addition of any base (OH^-) will move the equilibrium in the direction of the formation of the chromate (CrO_4^{2-}) ion.

Hence, *chromates exist primarily in alkaline media, and the dichromates in acid solutions.*

For example, if a solution of potassium chromate is acidified with dilute sulfuric acid we can expect the reaction

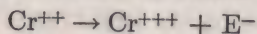


while the addition of dilute potassium hydroxide to a solution of potassium dichromate would cause the reaction

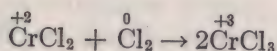


to take place.

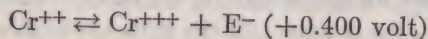
Chromates and Dichromates as Oxidizing Agents.—As mentioned previously, the chromous, Cr^{++} , compounds are reducing agents owing to the tendency of the Cr^{++} ion to gain positive valence by losing an electron, in order to attain the stable valence state of +3; *e.g.*,



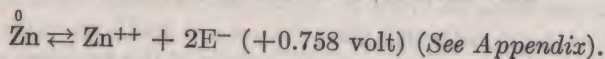
or



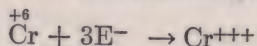
Consequently, in order to reduce a chromic ion to the chromous condition, we shall have to use a reducing agent that is a stronger one than is the chromous ion itself.



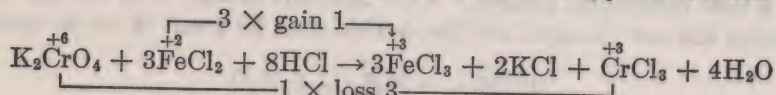
We meet with such a reducing agent in the case of metallic zinc in acid solutions, as for example Zn/HCl , since the oxidation-reduction potential of Zn is 0.758 volt.



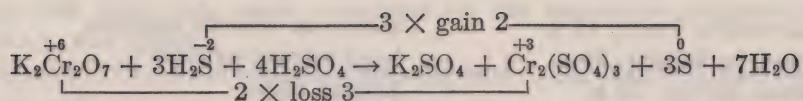
If then chromium shows a tendency to attain the valence state of +3, by the same reasoning by which we find chromous compounds to be strong reducing agents, we should expect the hexavalent chromium compounds to be good *oxidizing* agents. This will be due to the tendency of the hexavalent chromium to lose three positive valences (gain three electrons) as in the equation



As mentioned in the general discussion, we never meet with compounds of chromium in which the hexavalent element forms the positive ion. This is due to the non-metallic character of the element in this valence state. Hence an example of the above type of reaction would be



or

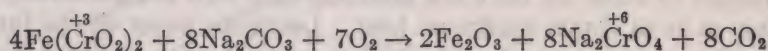


Actually if we acidified a chromate solution, we would have the dichromate formed first with subsequent reaction, as represented in the second equation.

EXPERIMENTAL

Since the greater part of the chromium produced is used as the chromate or the dichromate, it should be interesting to see how these compounds are prepared from the naturally occurring substances. The most common source of the element is ferrous chromite, $\text{Fe}(\text{CrO}_2)_2$, sometimes written as $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. Owing to the extremely high melting point (over $2000^\circ\text{C}.$) of this mineral, as well as to its indifference to attack by solutions, acids or bases, it is apparent that fusion with a flux will be necessary to bring about reaction.

As the chromium is in the acid radical, a basic fusion should be more effective than an acid one. Solid sodium hydroxide would be an efficient reagent, but in commerce a mixture of the cheaper basic reagents sodium carbonate and lime is used. During the fusion oxygen is absorbed from the air, so that the chromite is oxidized to the chromate.



Since neither time nor temperatures are available for the above process when working in the laboratory, we may bring about a similar reaction by using the less difficultly fusible oxide Cr_2O_3 and supply the oxygen by adding an oxygen rich salt, such as KNO_3 . Potassium carbonate is used as the basic flux. The principles involved, however, are identical with those of the commercial process.

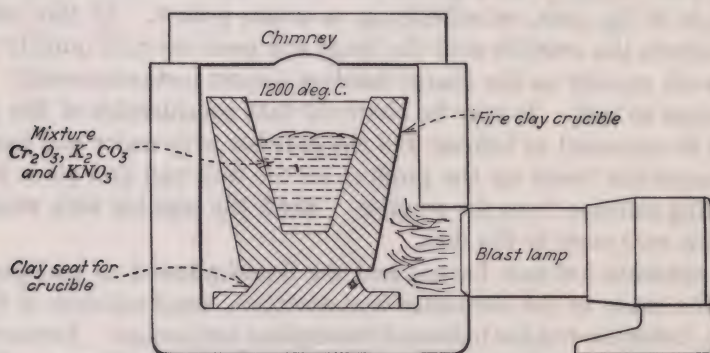


FIG. 19.—Preparation of potassium dichromate.

Apparatus:

- Fire-clay crucible
- Gas furnace¹ 100 ml. capacity
- 6-in. evaporating dish
- Iron pan
- Metal stirring rod
- Tongs
- Large filter

¹ Where such a furnace is not available, the fusion may be carried out in a 100-ml. iron crucible using a burner of the Meker type.

Materials :

Chromic oxide, Cr_2O_3 , 12 g.

Potassium carbonate, 30 g.

Potassium nitrate, 25 g.

Glacial acetic acid, CH_3COOH

Dilute hydrochloric acid

Stannous chloride solution

Lead nitrate solution

Litmus paper

Ice

Procedure.—Obtain the materials necessary and follow the directions *carefully*. Using the rough balances, weigh out the above portions of oxide, carbonate, and nitrate, mix them together thoroughly, and place the mixture in the crucible. This must not be more than two-thirds filled.

Note.—If the furnace to be used is not a small dental furnace, instructions as to its operation will be given by the instructor.

Place the crucible and contents in the dental gas furnace (Fig. 19), and have the iron pan close by. Turn the mouth of the blast lamp *away from* the furnace, turn the gas on, and light the jet. Adjust the flow so that you have a small luminous flame of about 4 in. in length. Air is then gently admitted until the flame just loses its luminescence, whereupon the burner mouth is inserted into the opening in the side of the furnace.

Note.—Never light the gas with the burner mouth in the furnace if you wish to avoid an explosion.

Allow the crucible to warm up for a few minutes, then turn the gas on to full pressure and adjust the air blast so as to obtain maximum heat. Leave the cover off the furnace and watch the crucible to see that the contents do not overflow when the gas evolution becomes vigorous. If there is any danger of this, reduce the air pressure or if necessary remove the blast lamp from the furnace until the effervescence dies down.

When the charge is completely molten and has ceased to effervesce, dip the *tip* of the stirring rod into the melt. Withdraw the rod and allow the portion of the substance adhering to the rod to solidify. If the color is still a dark green, the reaction is *incomplete* and heating must be continued until a sample of the melt, on solidifying, is bright yellow. At this point, with the blast still in operation, remove the crucible with the tongs and pour the melt quickly on to the iron pan. It is necessary to work rapidly as the charge hardens almost instantaneously.

Allow the crucible to cool. It may be observed that considerable of the product adheres to the crucible. This is recovered as follows: Fill the crucible with water and heat to boiling over a Bunsen flame. Meanwhile break up the product on the iron pan and place it in the large dish. Add to this the boiling solution from the crucible. Refill the crucible with water, reheat, and add the resulting solution *once more* to the dish.

The dish and contents are now heated and the liquid allowed to boil gently for 5 min. If the conversion of the oxide to the chromate was complete, total solution of the product will be obtained. A green, insoluble residue indicates incomplete conversion. Decant the liquid through a large filter, and add 10 ml. of glacial acetic acid *cautiously* to the filtrate. Evaporate the solution until crystals of the dichromate *begin* to appear. Another 5 ml. portion of acid is now added and the solution allowed to stand for a short time. Finally cool to 0°C ., or as low a temperature as is possible, and filter out the crystal meal that is formed. This is to be purified by recrystallization, dried, and weighed.

Record the weight of $\text{K}_2\text{Cr}_2\text{O}_7$ obtained.

EXPERIMENTS

1. To 5 ml. of $\text{K}_2\text{Cr}_2\text{O}_7$ solution add 5 ml. of dilute HCl and 10 ml. of SnCl_2 solution. Note the result and write the equation for the reaction.

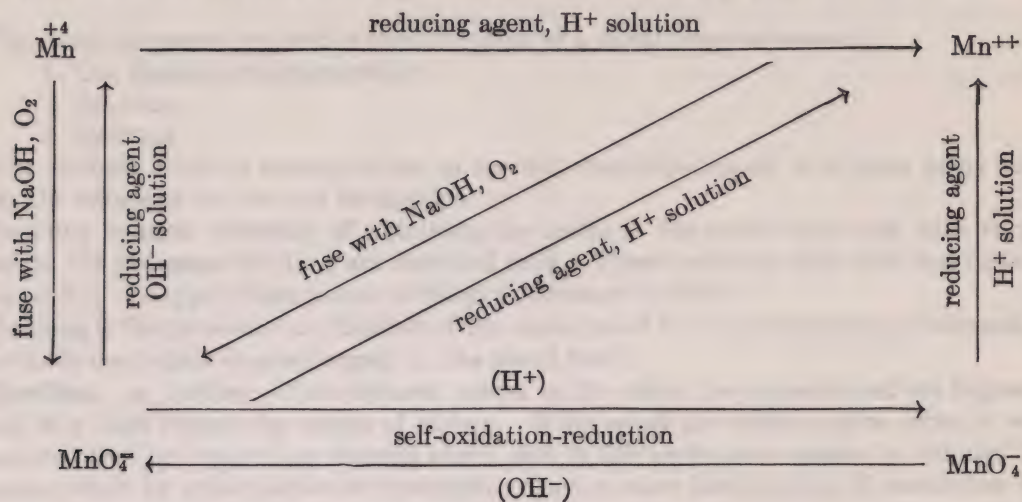
2. Dissolve a few crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ in water and add 2 ml. of lead nitrate solution. Test the mixture with litmus. Write the equation.

TREATMENT OF DATA

Calculate the percentage yield of potassium dichromate on the basis of the weight of chromic oxide used.

EXERCISES

1. Starting with $\text{Fe}(\text{CrO}_2)_2$, write equations for the successive preparations of K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}_2(\text{SO}_4)_3$, and CrSO_4 .
2. Starting with CrCl_2 , write equations showing how CrCl_3 , Na_2CrO_4 , and $\text{Na}_2\text{Cr}_2\text{O}_7$ may be successively prepared.
3. From the above reactions, indicate by means of a diagram how the various valence states of chromium may be obtained from one another, using as an example the diagram listed below showing how the various compounds of manganese may thus be prepared.



ASSIGNMENT 17

METALLURGY. THE PREPARATION OF METALLIC COPPER AND LEAD

The usual processes involved in the extraction of a metal from its ores are:

1. Ore dressing or concentration
2. Smelting
3. Refining

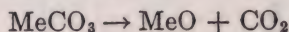
The methods used for concentrating an ore will naturally depend on a great many factors, such as the nature of the ore and its location.

Smelting consists primarily of obtaining the metal in the crude state and with very few exceptions the processes involved are chemical ones. These methods vary with the metal and also depend on the type of compound in which the element is found.

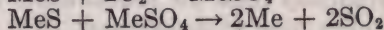
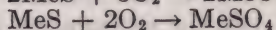
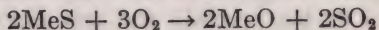
Refining is the process of purification of the crude metal from contaminating substances, and the methods used again depend largely on the metal itself.

Smelting. a. Oxides.—If the element occurs as the oxide, the concentrated ore is generally reduced in a blast furnace by means of carbon. If we recall the electromotive series, it will be remembered that no oxide of an element above zinc in this series may readily be reduced to the elementary state by either carbon or hydrogen. On the other hand, oxides of metals low in the series may be reduced simply by heating. It will be noticed, however, that the majority of useful metals fall into the class that forms oxides which may be reduced by means of carbon.

b. Carbonates.—If the ore is a carbonate, it is usually calcined to the oxide; *viz.*,



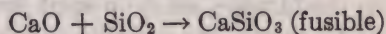
c. Sulfides.—Sulfide ores are generally roasted in the air to the oxide or sulfate, according to the reactions



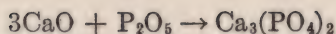
Usually the oxide is obtained as the product, although the metal or sulfate may also be formed in some cases. From the above reactions it is evident that the reduction of the oxides to the metals is one of the most important of metallurgical processes.

Smelting of Iron.—Among the more important metals are iron, copper, and lead. The chief ore of the former is the oxide, whereas the sulfide occurs more frequently in the latter cases. The smelting of all three, however, may be brought about by the reduction of the oxides by means of carbon.

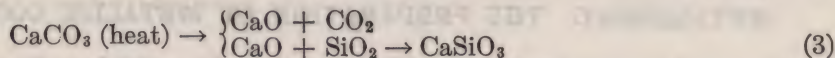
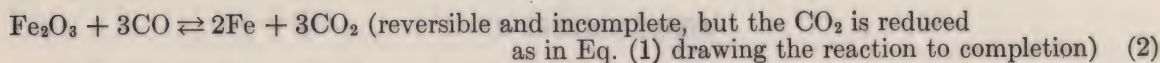
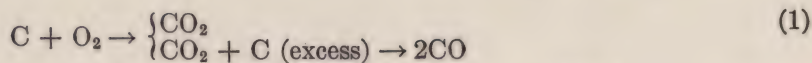
Iron ore, Fe_2O_3 , etc., is usually contaminated with large amounts of the acid oxide SiO_2 . Both of these oxides have high melting points, and if simply heated with carbon would be subjected to little or no reduction. In such cases it is necessary to make use of a flux. When there is an impurity such as silica (SiO_2) which can be converted into a more easily fusible compound, that reaction is used to advantage. SiO_2 being acidic reacts with basic fluxes more readily than with acidic ones, forming the readily fusible silicates; *e.g.*,



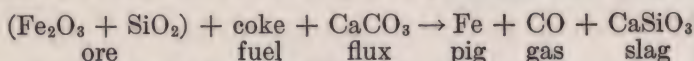
Since CaO is easily obtained from CaCO_3 which is a cheap reactant, limestone is one of the most commonly used fluxes for siliceous materials. If other acidic oxides are present, such as P_2O_5 and As_2O_3 , they are also attacked by the basic oxide and form part of the slag; *viz.*,



Siliceous materials are therefore usually roasted to the oxides and then smelted with limestone and carbon. The reactions that take place in the blast furnace may be divided into three classes,



The general reaction in the case of iron may be represented by the equation



EXPERIMENTAL

PART A. THE METALLURGY OF LEAD

Apparatus:

- Fire-clay crucible
- Iron pan
- Gas furnace
- Tongs
- Iron mortar and pestle

Materials:

- Lead oxide, 30 g.
- Powdered wood charcoal, 4 g.
- Anhydrous sodium sulfate, 30 g.

Procedure.—Weigh out the above reagents on the rough balances, powder the charcoal well, and then add all three substances to the crucible and mix *thoroughly*. Place the crucible and contents in the gas furnace and gradually raise the temperature to yellow heat. (For directions regarding the operation of the furnace refer to Assignment 16.)

Maintain this temperature until the reaction mixture is molten and then allow it to bubble for another 5 min. The charge *must not* be allowed to harden in the furnace, as when this occurs, reoxidation of the metal sets in. Remove the crucible with the liquid charge and pour it quickly into the iron pan which must be thoroughly dry. When the charge has cooled, break it up and separate the lead from the slag. Weigh your product.

PART B. THE METALLURGY OF COPPER

Materials:

- Black oxide of copper, 20 g.
- Powdered wood charcoal, 4 g.
- Anhydrous sodium sulfate, 30 g.

Procedure.—Proceed as in the case of lead, using the crucible from the previous experiment. When the crucible is removed from the furnace, set it on some *fireproof* material and leave it until the charge has hardened. This is to permit the metallic copper to settle to the bottom of the crucible, where it should solidify into a button.

Meanwhile, fill the sink with water and then immerse the still hot crucible and contents in the water, plunging it well below the surface and maintaining a firm hold on it with the tongs.

Stand well back from the sink during the quenching and do not remove the crucible until ample time has been allowed for the charge to have cooled completely.

When the crucible is cool enough to handle, break it in the iron mortar and remove the copper button. Clean and polish it, and then weigh.

TREATMENT OF DATA

Calculate the percentage yield on the basis of the weight of oxide used.

EXERCISES

1. Of what did the slag consist in the above experiments? In answering this question take into consideration appearance and odor, if any.

2. In the smelting of sulfide ores, vast quantities of sulfur dioxide are produced. Outline a method for the conversion of this substance into an important product.

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF CHEMISTRY
CHICAGO, ILLINOIS 60637

TO THE EDITOR:
I am writing to you to inform you of the results of my research on the properties of the new material I have discovered. The material has been found to have a unique set of properties that make it a promising candidate for a variety of applications. I am currently working on a paper describing these results and will be submitting it to a journal in the near future. I would be pleased to discuss these results with you further.

Sincerely,
[Name]

Enclosed for you are two copies of the paper. One copy is for your personal use and the other is for the library. I would be pleased to provide you with a third copy if you would like. I am also enclosing a copy of the abstract of the paper for your information.

I am looking forward to hearing from you soon. Please let me know if you have any questions or if you would like to discuss the results of my research further.

Very truly yours,
[Name]

I am writing to you to inform you of the results of my research on the properties of the new material I have discovered. The material has been found to have a unique set of properties that make it a promising candidate for a variety of applications. I am currently working on a paper describing these results and will be submitting it to a journal in the near future. I would be pleased to discuss these results with you further.

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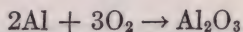
I am looking forward to hearing from you soon. Please let me know if you have any questions or if you would like to discuss the results of my research further.

ASSIGNMENT 18

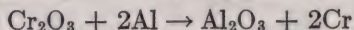
METALLURGY. METALS BY THE GOLDSCHMIDT PROCESS

The metals manganese and chromium are not easily prepared by reduction of the corresponding oxides with carbon (see Assignment 17). This is due in part to the stability of these oxides; *i.e.*, the metals are high in the electromotive series. The chief difficulty, however, lies in high melting points of the metals, for manganese 1230°C. and for chromium 1615°C. In order to separate a metal from slag and other materials, it is necessary to reduce the oxide at a temperature higher than the melting point of the metal.

These difficulties may be surmounted by the use of metallic aluminum as a reducing agent. Aluminum is itself high in the electromotive series, and further in its interaction with oxygen an extremely high temperature may be reached. The reaction



evolves a great deal of heat, 380,200 calories for every mole of oxide formed, and reactions of similar vigor take place between aluminum and many metallic oxides; *e.g.*,



The reaction mixture requires to be ignited, *i.e.*, heated up in part to a sufficiently high temperature to start a vigorous reaction. This is easily done by oxidizing some of the aluminum with a powerful oxidizing agent such as barium peroxide. A mixture of barium peroxide with granular aluminum is known as *fuse powder* and may itself be ignited by a burning strip of magnesium ribbon.

Since the above process can be carried on without the extensive equipment necessary for furnace reduction of metals, it forms a convenient method of obtaining pure metals in small quantities. Applied to iron it forms a means of welding "in place." The charge is fired and the molten iron is allowed to run directly on to the junction to be welded. A mixture of iron oxide and aluminum is sold under the name of *thermite*.

EXPERIMENTAL

Either manganese, chromium, or iron is to be prepared in this experiment. The oxides must be powdered and should be thoroughly dried before use. In the case of manganese, the dioxide MnO_2 must be heated to form the lower oxide Mn_3O_4 otherwise the reaction would be too violent, whereas with chromium the reaction should be stimulated by the addition of potassium dichromate which acts as a powerful oxidizing agent.

Apparatus:

Fire-clay crucible, 100 ml. capacity:
Iron pan
Pail of sand

Materials:

Manganese dioxide, 65 g.

or

Fe_2O_3 , 45 g.

or

Cr_2O_3 , 50 g.

Granular aluminum, 20 g.

Fuse powder, $\frac{1}{2}$ g. Al, and 5 g. BaO_2

$\text{K}_2\text{Cr}_2\text{O}_7$ (in case of Cr), 10 g.

Magnesium ribbon

Procedure.—Weigh out the quantities of materials on the rough balances. Heat the oxide in the iron pan to dull-red heat and keep it about this temperature for 5 min.

Mix the charge of oxide and aluminum thoroughly in a mortar. In the case of chromium, melt the $\text{K}_2\text{Cr}_2\text{O}_7$ in an iron pan and let it cool. It is then pulverized and mixed with the charge.

Take approximately one-half of the fuse powder, and mix it with twice its volume of the main charge. Hold a small test tube in the middle of the clay crucible and pack the charge around it, thus leaving a hole in the middle on removing the test tube. Into this hole pour the mixture of fuse powder and charge, and fill it up with the rest of the fuse powder, which should also be spread over the top of the whole of the mixture in the crucible. Insert a strip of magnesium ribbon into the fuse powder, and imbed the crucible in a pail of dry sand *under the hood*.

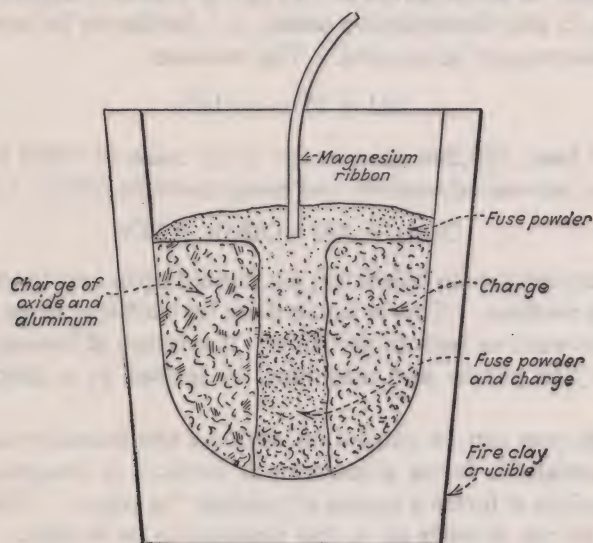


FIG. 20.—The Goldschmidt process.

Start the reaction by lighting the magnesium ribbon with a gas flame. Keep away from sparks and shield the eyes against the intense light given out in the reaction. When the crucible has cooled somewhat, remove it with a pair of tongs and quench it in water. Break the crucible and separate the button of metal. Clean it and weigh.

TREATMENT OF DATA

Write the equation for the reaction and calculate your percentage yield on the basis of the weight of oxide used.

EXERCISES

1. What would be the result of using chromite, $\text{Fe}(\text{CrO}_2)_2$, instead of Cr_2O_3 in the above preparation?
2. How might an alloy of manganese and iron be prepared by the Goldschmidt process?
3. List the important uses of the metals chromium and manganese.

SECTION C

REACTIONS OF ELECTROLYTES

ASSIGNMENT 19

ELECTROLYSIS. FARADAY'S LAWS

Many years before Arrhenius brought forward the theory of ionization in solution, the phenomena of electrolysis were well-known and had received considerable study. By 1834 Michael Faraday had established the laws governing this process, which may be stated under two heads:

I. The amount of chemical change at the electrodes is proportional to the amount of electricity passing through the circuit.

II. The same quantity of electricity produces quantities of the products which are proportional to their *equivalent weights*.

In the light of our present-day knowledge of ions and electrons, we find it possible to explain these regularities quite satisfactorily. Thus the process of conduction of electricity through the solution is carried on by the movement of the ions, the positive or *cation* traveling in one direction, and the negative or *anion* in the opposite direction. Since the anions have an excess of one or more electrons and the cations a corresponding deficiency, the electron stream coming from the battery or generator is ferried across the solution in the following manner. The waiting electrons on the cathode are seized by the incoming cations to produce neutral atoms, and, since electricity cannot pile up anywhere in the circuit, as the cations are being discharged at the cathode, anions are giving up their electron loads to the anode, forming likewise neutral atoms, and so the transfer of electrons is complete. The electrons which appear at the anode are *not*, however, the same individuals as those which left the cathode. The latter have become part of neutral atoms, while the former belonged originally to the ions of the electrolyte. Nevertheless, there is effected a continuous passage of electrons around the circuit.

Faraday's first law is then easy to understand. The amount of electricity passing must depend on the number of ions discharged at the electrodes, *i.e.*, the extent of chemical reaction.

For the second law we have to remember the connection between valence and gain and loss of electrons. Thus hydrogen has a positive valence of 1, since its atoms tend to lose one electron leaving the proton which in water solution forms the *hydronium* ion H_3O^+ . Copper has a positive valence of 2 and forms doubly charged positive ions Cu^{++} . Similarly, the negative ions carry as many electrons in excess as the negative valence of the radical or electronegative element.

We note that equivalent quantities of all ions must be associated with the same number of electrons, since we base equivalent weights on unit valence. Thus it is clear that the weights of substances which are liberated at the electrodes by the same quantity of electricity must be proportional to their equivalent weights. Consequently when 1.008 g. of hydrogen are liberated from a solution of hydrochloric acid, we obtain at the same time 35.457 g. of chlorine. If the same current is passed through solutions of cupric sulfate and silver nitrate, there are deposited 31.78 g. of copper and 107.88 g. of silver, while from each of these solutions 8 g. of oxygen are evolved.

The ordinary unit of quantity of electricity is the coulomb, which is the amount of electricity transported when a current of 1 amp. flows for 1 sec. The number of coulombs required to produce one equivalent weight of each of the products of electrolysis must be constant as we have

seen, and this number is found to be 96,500. This amount of electricity may be considered as an equivalent amount or unit, and to it the name faraday has been applied, in honor of the famous investigator of electrolysis.

$$1 \text{ faraday} = 96,500 \text{ coulombs}$$

EXPERIMENTAL

In this experiment the object is to verify Faraday's laws by passing a current through two electrolytic cells in series, measuring the volume of hydrogen produced in the one and the weight of copper deposited in the other. As electrolytes we shall use sulfuric acid and copper sulfate. The current is to be measured and the value of the Faraday estimated.

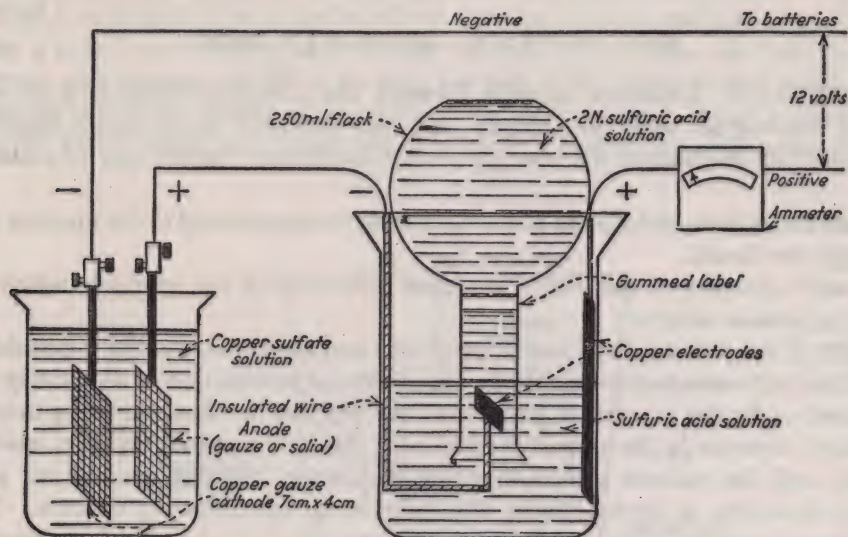


FIG. 21.—Electrolysis.

Apparatus:

- Large beaker
- 250-ml. flask
- Ammeter
- Thermometer
- Two pairs copper electrodes (see diagram)
- Connecting wires
- 12-volt battery
- 100-ml. graduate

Materials:

- 2N sulfuric acid
- Blue vitriol 10 g.
- Alcohol (for washing electrode)

Procedure.—Weigh the clean and dry copper-gauze electrode on the accurate balances. Dissolve the copper sulfate in about 200 ml. of water and place this in a 250-ml. beaker. Place about 300 ml. of 2N sulfuric acid in the large beaker and insert the electrodes. Make a mark on the neck of the 250-ml. flask and measure by means of a graduate the volume of water necessary to fill the flask up to this mark.

Fill the flask completely with 2N sulfuric acid and invert it over the negative electrode in the large beaker, so that the liquid level in the beaker is exactly at the mark. Set up the rest

of the apparatus as shown in the diagram (Fig. 21). The electrodes in the copper sulfate solution should be parallel and directly opposite one another at a distance of about 1 in.

Close the circuit momentarily and observe the current. This should be between 1 and 1.5 amp. If this is not the case, with the battery disconnected, adjust the distance between the electrodes in the large beaker and test again.

Now close the circuit and *note the exact time*. Record the ammeter reading and keep the current as nearly constant as possible by making small adjustments of the electrodes when variation occurs. Keep the liquid level constant in the large beaker by siphoning off the excess solution, as it is forced from the flask.

When the hydrogen collected has forced the liquid level inside the flask down to the mark on the neck, open the electrical circuit and *note the time*. Measure the temperature of the solution in the large beaker.

Carefully remove the gauze electrode carrying the deposited copper, wash it, and let dry thoroughly in warm air. Weigh it accurately.

Record the barometric height. Replace the used sulfuric acid in the bottle provided.

TREATMENT OF DATA

1. Calculate the volume of hydrogen obtained at standard conditions, and its weight.
2. From the weight of copper obtained and the weight of hydrogen, calculate the equivalent weight of copper.
3. From the total time and the current, calculate the number of coulombs of electricity which passed through the circuit.
4. Using the weight of hydrogen obtained, calculate the value of the Faraday.

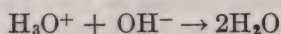
EXERCISES

1. Write the ionic equations for the reactions which took place during this experiment.
2. What difficulty might be encountered if copper nitrate was used in place of copper sulfate?
3. The copper electrodes are replaced by zinc. What additional reactions now take place?

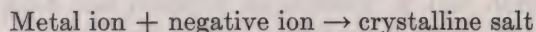
ASSIGNMENT 20

REACTIONS BETWEEN ACIDS AND BASES. NEUTRALIZATION TITRATION

A very important type of reaction is that in which an acid and a basic hydroxide neutralize each other to form water and a salt. Since we believe the essential property of an acid to be that of providing protons, while that of a basic hydroxide is to provide hydroxyl (OH^-) ions, we see that neutralization really means the union of two kinds of ions to form the practically undissociated substance water, according to the equation



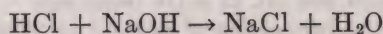
since each proton (H^+) combines with a molecule of water to form one hydronium ion (H_3O^+). The positive ion of the base and the negative ion of the acid usually remain as free ions in solution since most salts are completely ionized, and the reaction



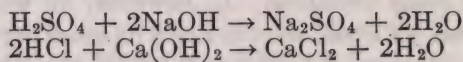
can take place only after the solution becomes saturated.

Thus there should be a great similarity between all neutralization reactions, and the principles we work out in the case of a particular acid and base should apply equally well to any acid reacting with any base.

Equivalent Weights.—On the quantitative side we can readily see that the acid must supply one hydronium ion H_3O^+ for every OH^- ion supplied by the base, if both acid and base are to be completely used up in the reaction. Thus in the case of an acid like hydrochloric which produces one proton for every molecule of HCl , and of a base like sodium hydroxide which supplies one OH^- ion, it is clear that one molecular weight of HCl will react with one molecular weight of NaOH ; viz.,



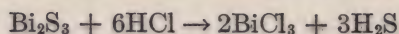
If, however, either acid or base supplies more than one characteristic ion per molecule, then the molecular proportions will no longer be one to one, as can be seen from the following equations:



In calculating quantities involved in these reactions, it is convenient to refer to the amount of acid or base which supplies just one H_3O^+ ion or OH^- in the equation. So instead of making our unit the molecular weight, we make it that weight of the acid which provides for reaction, one atomic weight of hydrogen in grams, and in the case of the base that weight which will react with one atomic weight of hydrogen i.e., the weight which provides 1.008 + 16.0 or 17.008 g. of OH^- ion. We see at once a relationship between these quantities and the equivalent weights of elementary substances, the standard in both cases being the atomic weight of hydrogen in grams. Hence we call these weights of acid or base, calculated on this basis, the *equivalent weights*, and we can see that the same reasoning would apply to a salt as well, since the *gram-equivalent weight of a compound is merely that weight which in a reaction supplies or is equivalent to 1.008 g. of hydrogen*. Thus the equivalent weight of HCl in a neutralization reaction is equal to 1.008 g. + 35.457 g. = 36.463 g., while that of $\text{Ca}(\text{OH})_2$ is equal to $\frac{1}{2}(40.07 + 2 \times 17.008)$ g. = 37.043 g. since that weight will react with 36.463 g. of HCl .

It turns out that the equivalent weight is equal either to the molecular weight or to some simple fraction of it. Thus for sulfuric acid, the equivalent weight is equal to $\frac{1}{2}$ H_2SO_4 in grams = 49.038 g., while the equivalent weight of phosphoric acid is $\frac{1}{3}$ H_3PO_4 in grams = 32.688 g.

Furthermore, the equivalent weight of bismuth sulfide is $\frac{1}{6}$ Bi_2S_3 in grams, since in the reaction:



six equivalents of hydrochloric acid react with one molecular weight of bismuth sulfide.

Normality.—Because of this extremely simple rule, *viz.*, that *one equivalent of a compound always reacts with one equivalent of another compound*, we find it convenient to express the concentrations of the solutions we work with in terms of the number of equivalent weights present in a liter of solution, instead of the number of molecular weights in a liter. Concentration expressed in this way is known as *normality* and a *normal solution contains one equivalent weight in 1 l. of solution*. For example, with hydrochloric acid this amounts to 36.463 g. of HCl per liter and is the same as a molal solution of HCl since the equivalent weight in this case is equal to the molecular weight. A normal solution of H_2SO_4 , on the other hand, contains 49.038 g. of H_2SO_4 per liter of solution which is only half as much as is contained in a molal solution, since the equivalent weight of H_2SO_4 is one-half of its molecular weight.

Solutions of other concentrations are described by using multiples or fractions of the normal solution. Thus we speak of 6 normal (6N) HNO_3 , meaning that the solution contains six equivalent weights of HNO_3 per liter of solution, or 0.457N AgNO_3 , in which the weight of silver nitrate per liter is 0.457 times the equivalent weight of AgNO_3 .

EXPERIMENTAL

The object of this experiment is to make up a solution of a definite normality and to use this solution in determining the concentration of another solution.

We can readily see from the foregoing that 1 l. of a normal solution of an acid will neutralize 1 l. of a normal solution of a base, since each contains one equivalent, and it follows that 10 ml. of this acid will neutralize 10 ml. of the base, since this volume contains ten one-thousandths or one one-hundredth of an equivalent in each case. Thus,

10 ml. of 1.0N acid reacts with 10 ml. of 1.0N base

10 ml. of 2N acid reacts with 20 ml. of 1.0N base

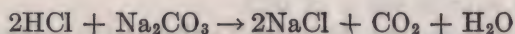
50 ml. of 0.5N acid reacts with 250 ml. of 0.1N base, etc.

We frequently make use of the properties of normal solutions in chemical analysis, and for this purpose we need solutions of definitely known normality. These are known as *standard solutions*. Thus the dilute sulfuric acid used in the laboratory is approximately 6N, which is a convenient concentration for many reactions. If, however, we wished to use this solution for quantitative analytical purposes, we would have to know its exact normality, (*i.e.*, 6.000N, 6.056N, 5.995N, etc.) or we could use solutions of 4.835N or 0.1992N, etc., the actual value of the normality being not so important as the accuracy with which we know that value.

In making up a standard solution, it is seldom possible to obtain an accurate concentration by weighing the solute and making it up in a definite volume of solution. The reason for this is that many of the compounds used are either hygroscopic or tend to evaporate so that it is difficult to obtain an accurate weight. Therefore the solution is made up to approximately the desired normality and then carefully analyzed to determine its exact normality. In this analysis we may make use of a substance which may be weighed accurately.

For example a solution of hydrochloric acid is made up approximately 1.0N and is analyzed by allowing it to react with sodium carbonate. 2.406 g. of Na_2CO_3 are weighed out and the acid slowly added until reaction is complete. If the volume of acid solution required is 45.1 ml., what is the exact normality of the acid?

Now from the equation



we see that the equivalent weight of Na_2CO_3 is one-half its molecular weight or 53 g. Therefore the fraction of an equivalent of Na_2CO_3 which we weighed out was 2.406/53 or 0.0453. Since

45.1 ml. of the acid solution reacted with this, that volume of solution must also contain 0.0453 equivalent of acid. The normality is therefore

$$\frac{1000}{45.1} \times 0.0453 = 1.006N$$

Now if we had a solution of any base of which we wished to determine the concentration, we could allow a definite volume of it (say 25 ml.) to react with sufficient acid for exact neutralization.

Thus, if 25 ml. of xN base neutralize 50 ml. of 1.006N acid,

$$\begin{aligned} 25 \times x &= 50 \times 1.006 \\ x &= \frac{50}{25} \times 1.006 = 2.012 \end{aligned}$$

The normality of the base is therefore 2.012.

Titration.—Analysis involving the use of standard solutions is known as *volumetric analysis*. The process of allowing a measured volume of solution to react is known as *titration*. For the purpose of measuring out definite quantities of standard solution we use an instrument known as the *pipette*. For the purpose of adding one solution to another in measured amount we use a *burette*. The stage in the process where the reaction is just complete is known as the *end point*. For the purpose of determining the end point of a reaction we make use of *indicators*. As indicators for neutralization reactions we make use of a number of organic dyes of which litmus is one. These compounds have the property of existing in two different forms which exhibit different colors; one form exists in acid solution, and when the solution becomes basic the other form is produced and the color changes. Thus if we are adding acid from a burette to a solution of a base, a small quantity of the indicator is placed in the basic solution, where it assumes its characteristic color. As long as the solution is basic, the indicator has the same color. When, however, the end point is reached and the solution becomes neutral, the addition of the next drop of acid causes the indicator to change color. It is obvious that the indicator must be very sensitive to an extremely small quantity of either acid or base, since we wish the color to change as close to the end point as possible, *i.e.*, when only a negligibly small amount of acid (or base) has been added in excess. Phenolphthalein is such an indicator, and we use it frequently in titration. In acid solution it exists as a colorless compound and turns pink when the solution is made basic.

Apparatus:

- Burette with pinch clamp
- 10-ml. pipette
- 500-ml. flask
- 100-ml. graduate
- Two 250-ml. beakers
- Stirring rod

Materials:

- Sodium hydroxide (pellets)
- Oxalic acid
- Vinegar
- Phenolphthalein solution

Procedure. *a. Preparation of a Standard Solution of Sodium Hydroxide.*—Calculate the weight of sodium hydroxide required to form 500 ml. of 0.1N solution and weigh out this quantity using the rough balances, *on a watch glass*. Dissolve the sodium hydroxide in approximately 50 ml. of water in a beaker. Meanwhile calibrate your 500-ml. flask by pouring into it 500 ml. of water measured by means of the graduate and pasting a strip of gummed paper opposite the bottom of the meniscus (curved surface of the water). Now empty the flask and pour into it the solution of sodium hydroxide, rinsing the beaker with a little water (wash bottle) and pouring

this into the flask. Fill the flask to the 500-ml. mark with water, cork, and shake to mix the solution thoroughly.

b. *Standardization of the Solution by Titration against Oxalic Acid.*—Calculate the weight of crystallized oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, required to react with 25 ml. of 0.1N solution. Weigh out *accurately* on the quantitative balance two portions of oxalic acid of approximately this weight. Dissolve these immediately in about 50-ml. portions of water in two beakers, and mark each beaker with the weight of oxalic acid present. Now wash out the burette, noting whether the water runs down the sides readily. If it tends to stick or form drops, wash the burette with a little soap solution and then rinse with water. Test the pinch clamp to see that there is no leak. Drain the burette completely, then add 10 ml. of the sodium hydroxide solution, shake it up well, and allow it to drain into the sink. This is to prevent the solution from becoming diluted by the water which remained on the walls of the burette after washing. Now fill the burette approximately to the zero mark with sodium hydroxide solution, and *make sure the tip is full*. Add 2 drops of phenolphthalein solution to the oxalic acid solution in the beaker and place it under the burette on a piece of white paper. Read the position of the bottom of the meniscus in the burette and record this value to the nearest 0.05 ml. Allow the sodium hydroxide solution to run slowly into the beaker, holding the pinch clamp of the burette in the left hand and stirring the solution in the beaker continuously with the other. After 20 ml. of solution have run in, close the clamp somewhat and allow the solution to come from the burette *drop by drop*, continuing the stirring. Stop when the solution in the beaker shows the first faint-pink color throughout its whole volume. Read the burette and record the reading.

Repeat the titration using the other oxalic acid solution.

c. *Determination of the Acid Concentration of Vinegar.*—Measure out with the graduate about 25 ml. of vinegar. Wash your pipette and rinse it with a few cubic centimeters of vinegar. Now draw vinegar into the pipette until the liquid is just above the level of the graduation mark. Place the first finger of the hand which is holding the pipette over the end to prevent the liquid from running out, then rotate the pipette slightly with the fingers until the bottom of the meniscus just reaches the mark. Press the forefinger down tightly to prevent further loss, carry the pipette over a beaker, then allow the liquid to run out. Do not blow the last drop of liquid out of the pipette, but just touch the tip to the inside of the beaker until no more will run out. You will then have exactly 10 ml. of vinegar in the beaker. Add about 50 ml. of water to the vinegar and 2 drops of phenolphthalein solution, and titrate with the sodium hydroxide solution in the same way as before. Record the burette readings.

Repeat the titration with a second 10-ml. portion of vinegar.

TREATMENT OF DATA

1. Obtain the volumes of sodium hydroxide solution used in each titration. From the titrations with oxalic acid, calculate the normality of the sodium hydroxide solution in each case, and take the average as the true value.

2. From the normality of base solution and the data obtained in the titration of vinegar, calculate the normality of the vinegar in the two experiments, and obtain the average value.

3. The acidity of vinegar is due to the presence of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. Calculate the weight of acetic acid present in 100 ml. of the vinegar you have used.

EXERCISES

1. Why is it not necessary to measure accurately the volume of water used to dissolve the oxalic acid?

2. Would it be possible to make up a standard solution of oxalic acid by direct weighing? Of hydrochloric acid?

3. If the end point is overrun in the titration of the vinegar so that the solution becomes a deep pink, can you suggest a means of saving the experiment?

ASSIGNMENT 21

IONIZATION OF ACIDS AND BASES. HYDROLYSIS

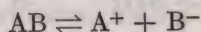
In Assignment 20 we studied the quantitative relationships involved in reactions such as neutralization. No mention was made, however, of the fact that acids and bases show different capabilities for producing their characteristic ions, the hydrogen ion and the hydroxyl ion, respectively.

Since the electrical conductivity of solutions of different acids and bases varies widely, even when we make comparisons under the same conditions of concentration, etc., we are forced to conclude that the extent or degree of ionization of these different compounds likewise varies. It is possible to calculate this *degree of ionization* from conductivity measurements.

Strong and Weak Electrolytes.—On comparing results from such experiments, we discover that all electrolytes fall, in general, into one of two classes. In the first class we have acids such as hydrochloric, nitric, perchloric, bases such as sodium and potassium hydroxides, and most salts. These compounds are so highly ionized in solution that in moderately dilute solutions only a negligible small fraction of the molecules appear to remain undissociated. Accordingly we shall consider these substances as being *completely* ionized under most conditions, which appears to be very closely in accord with their behavior. Compounds belonging to this class are called *strong electrolytes*.

On the other hand, there are a great many compounds in which dissociation appears to be far from complete, even in every dilute solutions. These are the *weak electrolytes* and comprise such acids as nitrous, sulfurous, and acetic, such bases as ammonium hydroxide and a few salts (mercuric chloride, etc.).

Here we must take into consideration the equilibrium

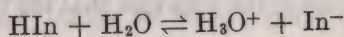


and the extent to which the neutral molecules are broken up to form ions may vary widely for different members of this class (see Appendix V).

The question naturally arises as to whether the degree of ionization of an acid or base has any effect on the quantity which is required for neutralization of another base or acid. If this was the case, our previous calculations with regard to the volumes of interacting solutions would have to be modified considerably. Fortunately, it is not necessary to do this, as the equivalent weight of an acid or base depends only on the number of units of replaceable hydrogen or hydroxyl in the gram-molecular weight. This is due to the fact that, as the ions combine to form water, the equilibrium is displaced, and a *continuous supply* of ions is produced by the acid or base until completely used up. Thus 10 ml. of 0.1*N* acetic acid will react with the same quantity of sodium hydroxide as 10 ml. of 0.1*N* hydrochloric acid does, although acetic acid is ionized only to the extent of about 1 per cent at this concentration, while hydrochloric acid is completely dissociated into its ions.

When, however, we consider the *experimental process* of titration, a difficulty arises in the case of weak acids and bases. To understand this, we must investigate more closely the behavior of the *indicators* used to determine the end point of such reactions.

Indicators.—These indicators, as we have seen, consist of certain organic compounds which under certain conditions show distinctive colors. These compounds may themselves be considered as very weak acids ionizing as follows:



where In^- represents the negatively charged organic radical. The ion In^- shows a color which is different from that of the molecule HI_n . Thus with methyl orange HI_n is red and In^- is yellow, while with phenolphthalein HI_n is colorless and In^- is pink.

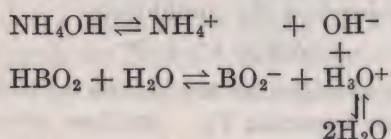
The equilibrium shown above will be disturbed if hydronium ions are removed from, or added to, the solution containing the indicator, in accordance with the **mass law**. Thus in a solution containing hydrochloric acid and phenolphthalein, the equilibrium will be shifted to the left due to the H_3O^+ ions from the HCl , and the colorless form HI_n will predominate. If now we neutralize the acid with $NaOH$ thus removing H_3O^+ ions to form H_2O , the equilibrium will be displaced to the right and the presence of the In^- ions will give a pink color to the solution.

It is obvious that a good indicator must be very sensitive to changes in the H_3O^+ ion concentration of the solution; *i.e.*, a small excess or deficiency of H_3O^+ ions must make an observable change in the equilibrium, and the color change should take place very near the neutral point. We say that a solution is neutral when the concentrations of H_3O^+ ions and OH^- ions are the same as those of pure water. The value of these concentrations is by no means zero, since water itself is ionized to a slight extent into an equal number of H_3O^+ and OH^- ions. At room temperature these concentrations amount to about 1×10^{-7} mole per liter, so that $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ M.

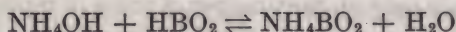
Most indicators do not change color exactly at the neutral point. Thus phenolphthalein does not turn pink until the H_3O^+ ion concentration has been reduced to 1×10^{-9} M (by addition of OH^-) and methyl orange turns from red to yellow while the H_3O^+ ion concentration is as high as 1×10^{-5} M. Litmus shows a gradual change of color in the neighborhood of the neutral point but is not suited for exact experimental work.

These deviations are unimportant in many types of titration especially in the case of neutralization of *strong* acids with *strong* bases, because a very slight excess of acid or base will usually produce the desired color change. Thus the H_3O^+ ion concentration in 10 ml. of water will change from 1×10^{-7} to 1×10^{-5} M on the addition of only $\frac{1}{1000}$ ml. of 0.1N HCl .

Weak Acids and Bases.—In titrations involving *weak* acids and bases, the neutralization process must be considered as a set of opposing equilibria, as shown in the following example,



As a result, the reaction will be incomplete, even when equivalent quantities of the acid and base have been mixed. Thus,

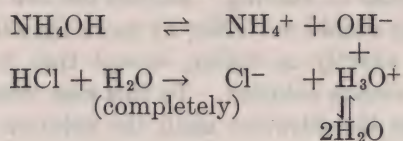


and the position of equilibrium will be determined by the relative degrees of ionization of NH_4OH and HBO_2 on the one hand, and H_2O on the other. Although the ionization of water is so slight, it is still sufficient to play a considerable part in the above equilibrium. Thus the above reaction is only about 50 per cent complete, owing largely to the very slight ionization of boric acid, HBO_2 .

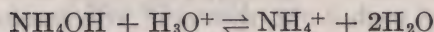
Obviously it would be useless to attempt to determine the total amount of either boric acid or ammonia present by means of titration, and in general, titrations involving weak acids and weak bases are usually avoided.

When we are dealing with the reaction between a *strong* acid and a *weak* base, or a *strong* base and a *weak* acid, the difficulty discussed above comes into play to a lesser degree, and we can avoid it almost entirely by making use of the very fact that the indicators do not in general change color exactly at the neutral point.

Thus in the reaction between ammonium hydroxide and hydrochloric acid we have:



or



since the chloride ion plays no part in the reaction.

This means that when equivalent quantities of NH_4OH and HCl are brought together we still have present in the solution a certain amount of NH_4OH (un-ionized), and a certain amount of H_3O^+ ion, over and above the amount coming from the water itself.

If now the indicator is so chosen that its color change takes place when just that excess of H_3O^+ ions is present, then the end point will be accurately determined by the change in color. This is closely the case in the above reaction when we use methyl orange, and therefore no appreciable error is made when methyl orange is used in the titration. The use of phenolphthalein would produce an incorrect result, since this indicator would turn colorless when less than an equivalent quantity of HCl had been added to the NH_4OH .

Similar reasoning will show that for the reaction between a weak acid and a strong base, we would make use of phenolphthalein in preference to methyl orange to indicate more closely the point at which exactly equivalent quantities of acid and base have been brought together.

Hydrolysis.—It is a corollary to our reasoning in the last section that the salt formed from a weak acid and a weak base, for example ammonium borate, will react with water to some extent to give free acid and free base (largely un-ionized). The same will apply to a smaller degree to salts of which either the parent acid or base was weak, but not both. This type of reaction, which is seen to be the reverse of *neutralization*, is known as *hydrolysis*, and as a result the solutions formed by salts in water may not be neutral, as may be shown by the use of indicators.

EXPERIMENTAL

The present experiment is designed to test out these conclusions with regard to the use of indicators for titration of weak acids and bases, making use of the two common indicators, phenolphthalein and methyl orange.

Apparatus:

50-ml. burette
10-ml. pipette
two 250-ml. beakers
Stirring rod

Materials:

Standard hydrochloric acid, 0.1N	Aluminum sulfate
Standard sodium hydroxide, 0.1N	Ferric chloride
Acetic acid, approximately 0.1N	Sodium sulfide
Ammonium hydroxide, approximately 0.1N	Sodium hydrogen carbonate
Phenolphthalein solution	Sodium carbonate
Methyl orange solution	Sodium chloride

Noie.—Read over the directions for use of the burette and pipette in Assignment 20.

Procedure.—*a.* Fill the burette with standard sodium hydroxide solution, observing the same precautions as in Assignment 20. Pipette into each of two beakers 10 ml. of acetic acid solution. Dilute each to about 50 ml. and add 2 drops of phenolphthalein solution. Titrate each sample with the sodium hydroxide solution, taking as the end point the first appearance of a very pale

pink color which does not disappear on stirring. Record the two values of the volumes of sodium hydroxide solution used. These should not differ by more than 0.2 ml.

b. Repeat the experiment exactly as before, except that in place of the phenolphthalein solution use 2 drops of methyl orange solution. In this case remember that the color change is from red to yellow, so continue the titration until the solution takes on a pale-yellow shade. Record the volumes used.

c. Empty the burette and wash it out, then refill with standard hydrochloric acid. Pipette into each of the two beakers 10 ml. of ammonium hydroxide solution. Dilute to about 50 ml. and add 2 drops of methyl orange solution. Titrate each sample with hydrochloric acid, taking as the end point the first change of color from yellow to orange-red. Record the results.

d. Carry on an experiment similar to experiment c, using phenolphthalein instead of methyl orange. The end point here is when the red color has faded to a very pale pink. Record the results obtained.

Wash out the burette, discarding any standard acid left.

Do not return any unused standard solution to the supply bottles. These solutions must be kept free from contamination and dilution.

EXPERIMENT

Dissolve a few crystals of each of the following salts in 5 ml. of water in separate test tubes: $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , Na_2S , NaHCO_3 , Na_2CO_3 , NaCl . Test each solution with methyl orange and with phenolphthalein and note the colors. Explain the results and write equations for the ionic equilibria involved.

TREATMENT OF DATA

1. From the average values obtained in experiments *a* and *c*, calculate the normalities of the acetic acid and ammonium hydroxide solutions respectively.

2. Using the values obtained in experiments *b* and *d*, calculate the corresponding normalities of acetic acid and ammonium hydroxide solutions.

3. Assuming the results obtained in 1 as being correct, calculate the percentage error involved in:

a. Titrating acetic acid using methyl orange as indicator.

b. Titrating ammonium hydroxide using phenolphthalein as indicator.

EXERCISES

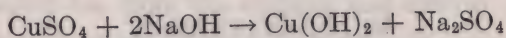
1. Predict whether solutions of the following salts will be acid, basic, or neutral: NaHSO_4 , NaHS , KCN , NH_4Cl , CuSO_4 , $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate).

2. From the position of the elements in the Periodic Table, which of the two compounds Na_3AsO_4 and Na_3SbO_4 should be the more stable towards water?

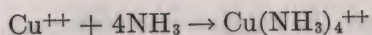
ASSIGNMENT 22

COMPLEX IONS. DETERMINATION OF AN EQUILIBRIUM CONSTANT

When sodium hydroxide solution is added to a solution of a copper salt, there is obtained a light-blue precipitate of copper hydroxide, according to the equation

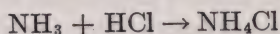


If, instead of sodium hydroxide, an excess of ammonium hydroxide is added, no precipitate is observed, but the solution assumes a beautiful deep-blue color, indicating the formation of some new substance in solution. Analysis shows that this blue color is due to the presence of a *complex ion*, formed by reaction between the copper ion and the ammonia of the ammonium hydroxide thus:

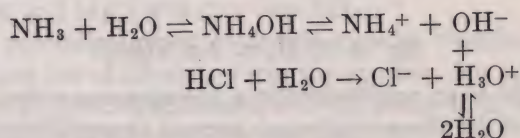


in which four molecules of ammonia have attached themselves to one ion of copper, much in the same way that water molecules are attached to a salt to form a hydrate (*e.g.*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

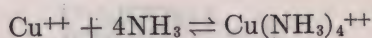
If an acid is added to the deep-blue solution the color fades and the solution resumes the paler blue color characteristic of the copper ion. Ammonia reacts with an acid to form a salt according to the equation



the equilibria involved being

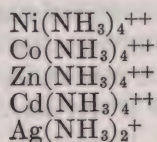


This experiment indicates that the reaction in which the complex ion is formed is reversible and should be written

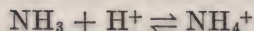


In presence of an excess of ammonia, however, the equilibrium is reached when only a very small quantity of free copper ions is left in the solution, since the concentration of these is not sufficient to produce a precipitate of copper hydroxide with the OH^- ions which are also present in the ammonium hydroxide solution. That there are still some free copper ions left may be proved by the addition of hydrogen sulfide to a solution containing the complex ion. Copper sulfide, which is much less soluble than copper hydroxide, is precipitated, indicating that, although the concentration of copper ions was too small to permit of the solubility product of copper hydroxide being reached, there were sufficient copper ions to exceed the value required for the much smaller solubility product of copper sulfide.

The property of forming complex ammonia ions is common to the ions of a number of metals. Thus we have the ions

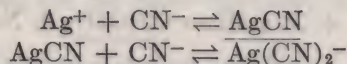


It is interesting to note that the ammonium ion itself may be considered as a complex ion formed by the proton thus:



and this ion is remarkable for its stability. The silver ion $\text{Ag}(\text{NH}_3)_2^+$ is also but little dissociated into silver ion and ammonia, since we can dissolve the insoluble silver chloride by adding ammonium hydroxide.

Other Complex Ions.—In addition to the complex ions formed with ammonia we have also a number of other types of complex ions. Many metals form complex negative ions with the cyanide ion $(\text{CN})^-$. Thus silver ion forms a complex $\text{Ag}(\text{CN})_2^-$ which can be produced by the action of potassium cyanide on a silver salt; *e.g.*,

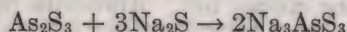


Copper ion likewise forms a cyanide complex, the cupric ion being first reduced to the cuprous, which then forms the ion $\text{Cu}(\text{CN})_3^-$. This ion is so little dissociated into Cu^+ and 2CN^- ions that the addition of hydrogen sulfide produces no precipitate of cuprous sulfide, although this compound is extremely insoluble.

Other types of complex ions are the halogen complexes; *e.g.*,



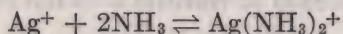
where the complex ion is SnCl_6^{2-} , and sulfide complexes formed by the sulfides of arsenic, antimony, and tin, by reaction with sodium or ammonium sulfides; *e.g.*,



The complex ion here is AsS_3^{3-} .

EXPERIMENTAL

The reaction



forms an interesting example of an equilibrium in a *homogeneous system*, and since we can readily determine the proportions of the three substances present at equilibrium, this forms a convenient example for testing the validity of the mass law as applied to such reactions.

The mass law expression for the equilibrium is:

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

in which K is the equilibrium constant of the reaction involving the formation of the complex ion, and the expressions in brackets denote the concentrations of the substances indicated.

The value of K indicates the extent to which the reaction has proceeded when equilibrium is established, and its reciprocal is known as the *complex constant*. Thus a very large value for K indicates that most of the silver is in the form of the complex ion, little free silver ion remaining. A very small value of K would show the reverse.

The experiment consists in preparing a series of equilibrium mixtures in which the proportions of the three components are different, determining in each case the three concentrations involved and, from these, several values for the equilibrium constant, which, of course, should be the same within the limits of experimental error.

The equilibrium is to be set up by mixing definite volumes of AgNO_3 and NH_3 solutions of known concentration. Remember that the negative ion (here NO_3^-) plays no part in the equilibrium so that we can consider the silver ion alone, and further we assume AgNO_3 in dilute solution to be completely ionized, so that if the solution is 0.05 molal in AgNO_3 it is also 0.05 molal in Ag^+ .

The key to the solution of the problem of determining the concentrations at equilibrium lies in the measurement of the free silver ion concentration $[Ag^+]$. This is obtained by an experimental application of the *solubility product* principle. If to the solution an ion is added which will form with the silver ion a little soluble compound as, for example, silver chloride, the precipitate can form only when the chloride ion concentration has reached the value such that

$$[Ag^+] \times [Cl^-] = k_s$$

where k_s is known as solubility product of silver chloride.

We add the chloride ion in the form of a solution of sodium chloride of known concentration and the saturation point is to be taken as indicated by the appearance of a faint turbidity due to the formation of a trace of solid silver chloride. Further addition of sodium chloride would, of course, remove the silver ion from the solution and destroy the equilibrium involving the complex ion, so that the above stage should not be overrun.

The value of $[Ag^+]$ is now obtained from the above equation. For example, if our equilibrium mixture has a volume of 30 ml., and to it we add 10 ml. of 0.05 M NaCl solution (to produce turbidity), then we proceed as follows:

The total volume of solution is now 40 ml. and therefore the concentration of chloride ion present is

$$0.05 \times \frac{10}{40} M = 0.0125 M$$

The solubility product of AgCl is given as 1.6×10^{-10} at room temperature. Therefore

$$[Ag^+] \times 0.0125 = 1.6 \times 10^{-10}$$

from which

$$[Ag^+] = 1.28 \times 10^{-8} M$$

The concentrations of the other two substances present in the equilibrium can now be found by a simple calculation. We can obtain the total concentration of silver (as free and as complex ion) since we know the volume and concentration of silver nitrate used. The difference between total silver concentration and $[Ag^+]$ will give $[Ag(NH_3)_2^+]$.

Similarly the total concentration of ammonia may be calculated. Since two molecules of NH_3 are removed with one ion of silver to form the complex ion (see equation), it is easily seen that the value of $[NH_3]$, *i.e.*, the free ammonia, is equal to the total concentration of the ammonia minus *twice* the concentration of the complex ion $Ag(NH_3)_2^+$.

The three concentrations being known, K may then be calculated.

Apparatus:

Two burettes
10-ml. pipette
Beakers and stirring rod
500-ml. flask (calibrated in Assignment 20)

Materials:

Sodium chloride, solid	Copper nitrate solution
Silver nitrate solution, 0.1 M	Sodium carbonate solution
Ammonia solution, 0.4 M	Hydrogen sulfide water
Potassium chromate solution, approx. 0.5 M	

Procedure.—Calculate the weight of sodium chloride necessary for 500-ml. of 0.05 M solution. Weigh out this amount on the rough balances, dissolve it in a small quantity of water, and make up the solution to 500 ml. in your flask. Obtain and record the exact concentrations of the silver nitrate and ammonia solutions which are provided in the laboratory.

Standardize your sodium chloride solution as follows: pipette a 10 ml. portion of the solution into a beaker and add 1 ml. of the K_2CrO_4 indicator, then titrate with the standard silver nitrate

solution until a faint but permanent reddish tint appears. Record the volume of silver nitrate solution used. Repeat this titration as a check.

Now fill one burette with sodium chloride solution and the other with standard ammonia solution. Into a 250-ml. beaker, pipette 10 ml. of standard silver nitrate solution. Run into this 20 ml. of ammonia solution. Then add slowly from the burette sodium chloride solution with constant stirring until there is a slight but permanent turbidity in the solution in the beaker. *If this end point is overrun, add enough ammonia solution to dissolve the precipitate*, noting the volume added, and again titrate with sodium chloride. Record the total volume of ammonia solution used, and the volume of sodium chloride solution added. Now add 10 ml. more of the ammonia solution and titrate as before. This will give a second set of data. Obtain a third by adding a further 10-ml. portion of ammonia and repeating the titration with the sodium chloride. Record all your data.

EXPERIMENT

To 5 ml. of copper nitrate solution add enough ammonium hydroxide to produce a clear but deep blue solution. Now add a few drops of sodium carbonate solution, note result, then add a few drops of H_2S water. Explain the results and write the equations for the reactions involved. (Copper carbonate is insoluble in water.)

TREATMENT OF DATA

1. From the average of the results obtained in the titration with silver nitrate, calculate the molality of your sodium chloride solution.
2. Obtain the total volume of the equilibrium mixture at the first end point, at the second, and at the third.
3. From these volumes calculate corresponding concentrations of the chloride ion in moles per liter, and also the molal concentrations of the total silver and total ammonia in each of the three cases. Tabulate these values.
4. Derive from the above data the concentrations of Ag^+ , $\text{Ag}(\text{NH}_3)_2^+$, and NH_3 in the three equilibrium mixtures.
5. Calculate the corresponding values of the equilibrium constant.

EXERCISES

1. Write the equations for the standardization of the sodium chloride solution, showing the formation of red Ag_2CrO_4 at the end point.
2. From the fact that the solubility of AgCl in water is 1.3×10^{-5} mole per liter, while that of Ag_2CrO_4 is 1.0×10^{-4} mole per liter, show why silver chromate is not precipitated until the chloride ion is practically completely removed.
3. What difference would be noted if the equilibrium mixture was titrated with sodium bromide instead of sodium chloride? The solubility product of silver bromide is 7.7×10^{-13} .

SECTION D

QUALITATIVE ANALYSIS

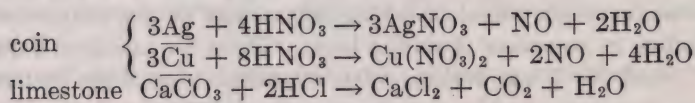
ASSIGNMENT 23

REACTIONS OF METALLIC IONS

Chemical analysis is of two types—*Qualitative* and *quantitative*. In *qualitative analysis* the nature of the elements and radicals composing the substance analyzed are determined without any attempt to measure the exact proportions of each; on the other hand, the methods of *quantitative analysis*, as the name indicates, lead to precise measurement of the quantities of the constituents present. The experimental procedure to be employed in these measurements depends usually upon what constituent is being measured, *e.g.*, the treatment of steel to determine carbon differs from the treatment to determine manganese. Hence a quantitative analysis is usually preceded by a qualitative determination of the elements present in the sample. Thus knowing what to look for in the unknown substance one can choose the most suitable method of arriving at the quantities present.

Qualitative Analysis.—The chief method of making a qualitative analysis is what may be called the “wet” method. Here the substance to be analyzed is first brought into solution with suitable reagents, and the solution is tested with a variety of reagents which produce characteristic reactions or precipitates, thus ensuring the separation and identification of the constituents present.

Preparation of the Solution.—This is not always a simple process as the original substance may not be soluble in water. Treatment with acids such as nitric or hydrochloric may produce the desired result as in the case of alloys of metals or carbonates.



In other cases the treatment may have to be more drastic, *i.e.*, evaporating with concentrated sulfuric acid or fusion at a high temperature with a basic flux. Tests of course must be made for any constituents which are likely to be lost as gases, etc., during the treatment, such as CO_2 in the second example.

The Process of Analysis.—If we are dealing with *inorganic* substances, the solution will contain the metals as positive ions and the non-metals either as negative ions or as part of negative radicals. The chemical reactions to be carried out are therefore *reactions between ions*, and the principles governing such reactions as precipitation (solubility product), complex ion formation, and general applications of the mass law to solutions of electrolytes will be involved.

With *organic* substances, special methods will have to be applied, and these will not be discussed here.

Separation of the Various Constituents.—The majority of the tests applied depend upon the formation of an insoluble (or only slightly soluble) compound. Since several constituents may form precipitates with the same reagent as in the case of the metal ions and hydrogen sulfide, methods of separation of one element from another must be used. It is not possible to apply specific tests to the first solution for every element present, and hence *separation* of the constituents always precedes *identification*. The constituent is first determined as belonging to a group having

similar properties with regard to insolubility of the compounds formed; these groups are then subdivided until the individual constituents are separate and may be tested for.

Object of the Experiments.—The object of the experiments described in this and succeeding assignments is not to describe in detail all the process of qualitative analysis. We shall confine ourselves to the study of the metal ions commonly found in many substances and comprising some 22 metals. We shall first investigate the separation of these constituents into groups, and then take as examples two of these groups, the analyses of which will be studied in detail in the assignments to follow.

The end to be achieved here is twofold. During the course in general chemistry you have been studying the reactions of electrolytes and the laws of ionization. These principles are put to practical application during the procedures of qualitative analysis, and the experiments will serve to fix more clearly in your minds the meaning and value of these laws. At the same time an insight will be obtained into that most important field of chemistry—analysis.

Laboratory Technique.—A good analyst is always neat and careful in his laboratory manipulation. If dirty apparatus is used and chemicals are spilled, the results of the analysis may bear no relation to the composition of the original substance.

Definite quantities of reagents are specified—usually by volume. You will appreciate the importance of controlling concentrations in view of the equilibrium principles involved, but it is not necessary to measure these quantities with the extreme accuracy of quantitative analysis, and a small graduated cylinder and rough balances (where weights are specified) are quite satisfactory.

Preliminary Tests and Unknown Solutions.—In order that the student may familiarize himself with the procedures to be used and the appearance and characteristics of the precipitates formed, a series of preliminary experiments are to be carried out making use of known constituents. For example, behavior of silver ion is studied in a series of experiments on silver nitrate. The results of these tests should be closely noted and also the conditions under which the tests are carried out.

After the completion of a section of preliminary work the student will obtain a sample of unknown composition which is to be analyzed making use of the procedures tested. For the purposes of this outline these “unknowns” will all be in the form of *solutions*.

Groups of Metal Ions (Cations).—Separation of the metals into groups may be effected by making use of some common property exhibited by all members of the groups. For example, one might group all the semi-metals together taking advantage of the amphoteric nature of their hydroxides and solubility in an excess of strong base. Thus, for example, if a solution containing Cr^{+++} , Al^{+++} , Fe^{+++} , and Ni^{++} was treated with an excess of sodium hydroxide, the elements could be divided into two groups—the metals precipitating as the hydroxides, the semimetals staying in solution in the anion.

We might also split the elements into groups according to their behavior with ammonia. Certain of the elements form complex cations with ammonia, for example Ag^+ , Cu^{++} , Cd^{++} , Ni^{++} , Co^{++} , and Zn^{++} . These complex cations do not form hydroxide precipitates, and hence if an excess of ammonia was added to the solution mentioned previously, the filtrate would contain the nickel solely, and the aluminum, chromium, and iron would be grouped together in the precipitate as the hydroxides. These processes have their places in the scheme of analysis which we are outlining. Separation into the main groups, however, depends upon the addition to the solution of certain reagents which cause the precipitation of selected groups of metals as insoluble compounds.

Group I: “Hydrochloric Acid Group” or Silver Group.—Elements whose chlorides are insoluble in water and dilute acids, *e.g.*, *lead*, *silver*, and *mercurous mercury*. (Note, then, that all other chlorides must be soluble.)

Group II: “Hydrogen Sulfide Group” or Copper-Tin Group.—Elements whose chlorides are soluble but whose sulfides may be precipitated from dilute acid solution by hydrogen sulfide, *e.g.*, *mercuric mercury*, *lead*, *bismuth*, *cupric copper*, *cadmium*, *arsenic*, *antimony*, and *tin*.

Group III: “Ammonium Sulfide Group” or Iron-Aluminum Group.—Elements whose chlorides are soluble and whose sulfides are not precipitated by hydrogen sulfide from dilute acid solu-

tions of concentrations sufficient to allow of precipitation of Group II, but whose sulfides or hydroxides are precipitated from solutions by hydrogen sulfide and ammonium hydroxide (ammonium sulfide), *e.g.*, manganese, iron, nickel, cobalt, aluminum, chromium, and zinc.

Group IV: "Ammonium Carbonate Group" or Alkaline Earth Group.—Cations forming soluble chlorides, sulfides, and hydroxides, but whose carbonates are insoluble, *e.g.*, barium, strontium, and calcium.

Note.—The student must not assume that these are the only elements forming little soluble carbonates. Under the conditions for precipitation of Group IV elements, practically all the cations of Groups I, II, and III would be precipitated, but these have been removed previously.

Group V: "Soluble Group" or Alkali Group.—These metals have no "group reagent" since their cations form chlorides, sulfides, hydroxides, and carbonates that are soluble either in water or in solutions containing ammonium salts, *e.g.*, magnesium, potassium, sodium, and the radical ammonium.

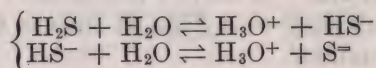
Note.—Many schemes of analysis place magnesium in Group IV by varying the group precipitation slightly.

It will be noted that the group reagents for Groups II and III are very similar, one being hydrogen sulfide in acid solution and the other hydrogen sulfide in alkaline solution (forming ammonium sulfide), and that in each case sulfides of the metals are precipitated (with a few exceptions). Differences in behavior of the two groups are dependent upon differences in solubility products of the sulfides, and emphasis is again laid on having the *proper concentration* (in this case, acidity) of the solutions.

Before precipitation from solution can begin the solution must be saturated with the substance involved, and the application of the mass law leads to the conclusion that the product of the concentration of the ions must reach some characteristic constant value. This constant is known as the "solubility product" of the compound and may be an extremely small number. Thus in the case of copper sulfide the value of $[Cu^{++}] \times [S^{=}]$ has been estimated at 8.5×10^{-45} . Since if we are testing for copper in the solution there is likely to be present an amount not much less than 0.001 mole per liter, we can see that the sulfide ion concentration required to initiate precipitation may be very small indeed (here $[S^{=}] = 8.5 \times 10^{-42}$ m.).

Manganese is a metal of Group III and for the sulfide we have $[Mn^{++}] \times [S^{=}] = 1.4 \times 10^{-15}$, which is several million times greater than that for CuS. Here a much higher concentration of sulfide ions is required.

When hydrogen sulfide is passed into water the following equilibria are set up:



Thus in accordance with the mass law an increase in H_3O^+ concentration (addition of another acid) serves to *decrease* the concentration of $S^{=}$ while addition of OH^- (from a base) will react with H_3O^+ and *increase* the concentration of $S^{=}$. Note that it is the $S^{=}$ ions themselves which are necessary to produce precipitates of metallic sulfides; HS^- or undissociated H_2S is of no value.

Now the sulfides of the Group II metals like copper all have solubility products which are considerably *smaller* than those of the Group III sulfides. The problem is therefore to adjust the $S^{=}$ concentration (by addition of acid) to such a value that the sulfides of the Group II metals will be completely precipitated, while at the same time the $S^{=}$ concentration is not high enough so that the solubility products of any of the group III metal sulfides is reached. After the precipitated sulfides are filtered off, the $S^{=}$ concentration is increased by addition of ammonium hydroxide, and the group III sulfides precipitate in their turn.

Calculations along these lines have shown that the correct value of the H_3O^+ concentration for Group II precipitation is 0.3 m., and the solution is adjusted to this value after precipitation of Group I.

The student must acquaint himself with the various groups and group reagents before attempting to analyze any solution for specific metals, and for this reason the first part of his work in analysis will be to test for the presence of the group rather than the individual cation.

EXPERIMENTAL

GROUP ANALYSIS

A. PRELIMINARY EXPERIMENTS

Precipitation of Group I Cations. 1. Solutions of either Ag^+ , Pb^{++} , or Hg_2^{++} may be used as representative of this group. AgNO_3 is generally used. Place 2 ml. of this solution (side shelf) in a clean test tube, dilute with 10 ml. of water, and then add dilute HCl (desk reagent) very slowly and with constant shaking as long as the precipitate forms. Pour through a filter paper and test the filtrate with a little more HCl . If a cloudiness appears the Ag^+ was incompletely precipitated so more HCl must be added and the resulting precipitate added to the former. Write an equation for the reaction.

2. Pass H_2S gas through the clear filtrate and note the result.

3. To the above filtrate add 1 drop of silver nitrate solution. What happens?

What would be the effect on an analysis of incomplete precipitation of the Group I cations as chlorides?

Precipitation of Group II Cations. 1. As an example of a cation occurring in this group we shall use Cu^{++} although solutions of Hg^{++} , etc., may be used. Take 2 ml. of a solution of copper nitrate and add 40 ml. of water. Add the same amount of HCl as for Group I. Is there a precipitate?

2. Now bubble H_2S gas slowly through the solution and when saturated, filter. Test the filtrate for incomplete precipitation by adding 60 ml. of water and passing more H_2S gas into it. Write an equation for the reaction.

3. Now make the solution alkaline with NH_4OH (litmus) and pass in more H_2S gas. Does more precipitate form?

4. Add 1 drop of Cu^{++} . What happens?

Would incomplete precipitation of Group II interfere with the test for Group III?

Precipitation of Group III Cations. 1. We shall use Mn^{++} as the example of this group. Take 2 ml. of a solution of $\text{Mn}(\text{NO}_3)_2$, dilute to 100 ml., and add 4 ml. of dilute HCl . Does a precipitate form?

2. Saturate the solution with H_2S . Is there a precipitate?

3. Now make the solution alkaline with NH_4OH (litmus test) and pass in H_2S gas again. Note the result and write the equation.

4. Filter and test the filtrate with $(\text{NH}_4)_2\text{CO}_3$ solution. Is there a precipitate?

5. Now add one drop of $\text{Ni}(\text{NO}_3)_2$ solution. What happens?

Precipitation of Group IV Cations. Use Ca^{++} as an example of this group. Take 2 ml. of a solution of $\text{Ca}(\text{NO}_3)_2$, dilute to 40 ml., and add 4 ml. of HCl . Saturate with H_2S . Add NH_4OH until alkaline. Add $(\text{NH}_4)_2\text{CO}_3$ solution, and if a precipitate does not form immediately heat just to boiling and set aside for twenty min. Note results, and write equations for any reactions you have observed to take place.

Precipitation of Group V Cations. Use Na^+ as representative in this case. Test a solution of NaNO_3 for Groups I, II, III, and IV. What is the result?

B. ANALYSIS OF AN UNKNOWN

Having become acquainted with the technique of the precipitation of the various groups, we can now analyze a solution for its constituents. We shall not attempt to isolate each cation but rather indicate what group or groups are present. Consequently such a test would yield the information as to whether or not one or all of the metals of that group are present. If a negative

test is obtained for any group, that indicates the absence of all the members of that group. If a positive test is obtained, we would have to analyze further to decide which ones were present.

For the present we shall content ourselves with reporting the presence or absence of the group. In the outline below the student must remember that the assumption is made that *all* groups may be present. If a negative test is obtained at any time, simply assume that that group is not present and carry on with the next procedure.

Procedure.—Obtain an “unknown solution” from the instructor.

P. 1. *Group I.*—To 10 ml. of your unknown add 4 ml. dilute HCl, shake, and allow the precipitate (if any) to settle. Add 1 drop more of HCl. If no further precipitation occurs, filter and treat the filtrate by P. 2. White precipitate indicates presence of Group I.

P. 2. *Group II.*—Dilute the filtrate from P. 1 to 100 ml. and saturate with H₂S. The precipitate indicates the presence of Group II. Heat almost to boiling and filter. Treat the filtrate according to P. 3.

P. 3. *Group III.*—Add NH₄OH to the acid filtrate from P. 2 until alkaline. Saturate with H₂S. Precipitate indicates Group III. Filter, reserving filtrate for P. 4.

P. 4. *Group IV.*—Make the filtrate from P. 3 acid with dilute HCl and evaporate by boiling in an open beaker or evaporating dish to about 25 ml. Filter out any precipitate, add NH₄OH until alkaline, heat to boiling, and then add 10 ml. (NH₄)₂CO₃ solution. Allow to stand 15 min. The precipitate indicates the presence of Group IV.

Since there is no group reagent for Group V the filtrate may now be discarded.

TREATMENT OF DATA

1. Write down the equations asked for and the answers to the questions in the preliminary experiments, marking each with the number of group to which it refers.

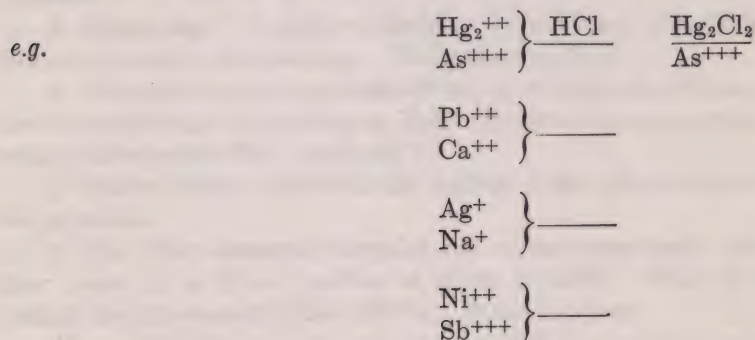
2. Prepare a tabular outline of your “unknown” analysis in accordance with Appendix IX. At the end of this make a summary of the results of the analysis, and write an equation for each reaction you observed, using typical metal salts as examples.

EXERCISES

1. In testing a solution for a “group unknown” a student finds Groups III and IV. If the solution actually contained only Zn(NO₃)₂, what error in technique has been committed?

2. What would be the effect of (a) too concentrated an acid solution (b) a basic solution if H₂S is passed into a solution containing both Groups II and III?

3. How would you separate the following cations from one another?



1. The Government of the United States of America, by and through the Secretary of the Interior, do hereby certify that the following is a true and correct copy of the original as the same appears in the records of the Department of the Interior, at Washington, D. C., this 1st day of January, 1900.

2. The said original is a copy of the report of the Commissioner of the General Land Office, made to the Secretary of the Interior, on the 1st day of January, 1900, and is a true and correct copy of the original as the same appears in the records of the Department of the Interior, at Washington, D. C., this 1st day of January, 1900.

3. The said original is a copy of the report of the Commissioner of the General Land Office, made to the Secretary of the Interior, on the 1st day of January, 1900, and is a true and correct copy of the original as the same appears in the records of the Department of the Interior, at Washington, D. C., this 1st day of January, 1900.

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ASSIGNMENT 24

GROUP I. THE SILVER GROUP

After the process of separation of the various groups of metals from one another, the precipitates consisting of compounds of Groups I, II, III, and IV and the filtrate containing Group V elements would be treated separately for the purpose of identifying the various metals present.

A series of preliminary experiments are therefore to be carried out using compounds of the metals of Group I,—*silver, lead, and mercurous mercury*. The results of these experiments are then to be applied to the analysis of this group.

Note.—Although this group is characterized by the insolubility of the chlorides, that of lead is appreciably soluble, and hence a part of the lead present will remain in the filtrate to precipitate as the sulfur in Group II.

Mercury also appears in Groups I and II but for a different reason. In the lower valence state mercury forms an insoluble chloride (Hg_2Cl_2) while HgCl_2 is quite soluble and therefore remains in the filtrate.

EXPERIMENTAL

A. PRELIMINARY EXPERIMENTS

1. Lead, Pb^{++} . 1. *Solubility of Lead Chloride*.—Dilute 2 ml. of $\text{Pb}(\text{NO}_3)_2$ solution to 10 ml. and add 4 ml. dilute HCl slowly, with shaking. Write an equation for the reaction.

Allow the precipitate to settle and decant the clear liquid. Add 10 ml. of water to the residue and heat to boiling. If the precipitate does not dissolve entirely, decant the liquid into another test tube and boil the residue with a further 10 ml. portion of water. Save the solution for (2). Note the result.

2. *Precipitation of Lead Chromate, PbCrO_4* .—To a portion of the solution from (1) add a few drops of potassium dichromate solution. What happens? Write the equation.

3. *Lead Sulfide*.—Saturate a second portion of the solution from (1) with H_2S . Write the equation.

2. Silver, Ag^+ . 1. *Silver Chloride*.—Dilute 2 ml. of AgNO_3 solution to 10 ml. and add 4 ml. dilute HCl slowly with shaking. Write the equation.

2. Decant the liquid and add 10 ml. of water to the residue. Heat to boiling, filter and test the filtrate for Ag^+ by passing in H_2S . Reserve the precipitate for (4). What happens? How could you separate Pb^{++} from Ag^+ ?

3. *Silver Sulfide*.—Dilute 2 ml. AgNO_3 to 25 ml. and pass in H_2S . What happens? Write the equation.

4. *The Silver-ammonia Complex Ion*.—Pour repeatedly over the precipitate of AgCl on the filter paper (1) a 10 ml. portion of dilute NH_4OH . What is the result? Write the equation. Acidify the filtrate with dilute HNO_3 . What happens?

Note.—The directions to "pour repeatedly" a solution over a precipitate in the filter paper may be carried out by catching the filtrate in a test tube. When the liquid has run through replace with an empty test tube while the liquid in the first is again poured onto the filter paper.

3. Mercury (mercurous), Hg_2^{++} . 1. *Mercurous Chloride*.—Dilute 2 ml. of $\text{Hg}_2(\text{NO}_3)_2$ solution to 10 ml. and add 4 ml. dilute HCl . Write the equation.

2. Test for the solubility of Hg_2Cl_2 in hot water as in the case of silver and note the result. Reserve any precipitate for (4).

3. *Mercurous Sulfide*.—Dilute 2 ml. of $\text{Hg}_2(\text{NO}_3)_2$ solution to 25 ml. and pass in H_2S . What happens?

4. *Reaction of Hg_2Cl_2 with NH_4OH* .—Treat the residue in the filter paper (2) with dilute NH_4OH . What is the result?

The product consists of a mixture of HgNH_2Cl (white) and Hg (black). Write the equation. How could you separate Hg_2^{++} from Ag^+ ?

B. ANALYSIS OF THE SILVER GROUP

After completion of the preliminary experiments, the student will obtain an "unknown" solution from the instructor. This solution will contain the cations of Group I only, and hence the filtrate from the group precipitation may be rejected.

Procedure. P. 5. *Precipitation of Group I*.—To 10 ml. of the unknown solution add 5 ml. dilute HCl , allow the precipitate to settle for a few minutes, and filter.

P. 6. *Lead*.—Boil 10 ml. of water and pour it through the filter containing the precipitate, collecting the filtrate. Add one drop of $\text{K}_2\text{Cr}_2\text{O}_7$ solution to this filtrate. A yellow precipitate of PbCrO_4 indicates Pb^{++} .

P. 7. *Silver*.—If a positive test is obtained for lead, and a residue still remains in the filter paper, pour through a fresh amount of hot water and test the filtrate with $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Repeat this until a fresh sample of the filtrate gives no test for lead. Reject the filtrates. To the residue remaining add 10 ml. dilute NH_4OH , and pour repeatedly through the filter. Make the filtrate acid (litmus) with dilute HNO_3 . A curdy white precipitate indicates the presence of Ag^+ .

P. 8. *Mercurous Mercury*.—If, during the addition of NH_4OH , above, the residue on the filter paper turns black, the presence of Hg_2^{++} is denoted.

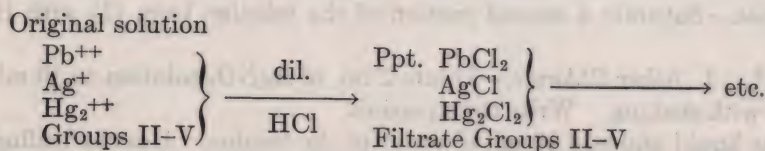
TREATMENT OF DATA

1. Write down the results of the preliminary experiments in order, using the numbers of the sections.

2. Make a tabular outline of your analysis, summarize, and write equations for all reactions which have taken place.

EXERCISES

1. Complete the following tabular outline of the analysis of Group I.



2. A student is given an unknown and obtains a large precipitate for Group I. The test for Pb^{++} is positive but considerable residue is left undissolved which does not test for either Ag^+ or Hg_2^{++} . Can you suggest an error in technique?

3. What other reagents besides HNO_3 might be used to precipitate AgCl from a solution containing $\text{Ag}(\text{NH}_3)_2\text{Cl}$? Write the ionic equations.

4. Outline a scheme of your own for the separation of the Group I cations from one another.

ASSIGNMENT 25

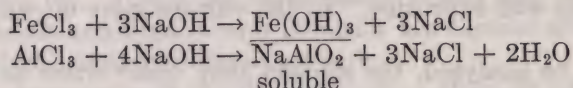
GROUP III. THE IRON-ALUMINUM GROUP. THE ALUMINUM SUBGROUP

The separation and identification of the elements of Group II is a little too difficult for an elementary course so as a second example of the methods used to separate and identify the individual metal ions we shall study the analysis of Group III. In the Group Analysis, the filtrate from Group II precipitation is made alkaline with ammonium hydroxide and saturated with hydrogen sulfide. Since the interaction of NH_4OH and H_2S produces $(\text{NH}_4)_2\text{S}$ we may consider *ammonium sulfide* as the group reagent. Under these conditions the sulfides of *iron, manganese, cobalt, nickel, and zinc* are precipitated, the solubility-products of these compounds being too large to permit of their precipitation with the extremely small sulfide ion concentration prevailing in the acid solution used for Group II. (See previous discussion.)

Two other elements are included in this group, *aluminum* and *chromium*, but these precipitate in the form of hydroxides instead of sulfides. The reason for this behavior is that the hydroxides of these elements are less soluble than the sulfides. Even if $(\text{NH}_4)_2\text{S}$ is added to the solution, the hydroxides of chromium and aluminum will be found in the precipitate, the solubility of the sulfides being sufficient to allow of complete hydrolysis (salts of a weak acid and weak bases). It is evident then that Al_2S_3 and Cr_2S_3 can only be prepared in the absence of water.

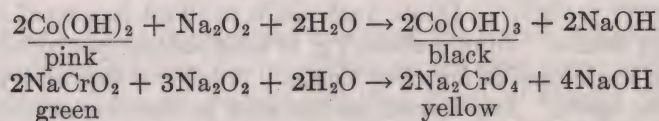
Separation of the Metals into Subgroups.—In order to simplify the analysis, the metal ions of Group III are first separated into two subgroups before identification of the individual metals is carried out. Advantage is taken of the fact that *aluminum, chromium, and zinc* are semi-metals and therefore form *amphoteric* hydroxides, while the remaining elements do not.

The first precipitate of sulfides and hydroxides is dissolved in acid, hydrogen sulfide is boiled out, and then sodium hydroxide is added in slight excess. The metals iron, manganese, cobalt, and nickel (the Iron subgroup) form precipitates of insoluble hydroxides, while aluminum, chromium and zinc (the Aluminum subgroup) remain in solution as anions, *e.g.*:



The precipitate may now be filtered out and the subgroups analyzed separately.

In actual practice, however, the separation is made more complete by adding a powerful oxidizing agent, sodium peroxide. This oxidizes any $\text{Fe}(\text{OH})_2$ to $\text{Fe}(\text{OH})_3$, $\text{Mn}(\text{OH})_2$ to hydrated MnO_2 , and $\text{Co}(\text{OH})_2$ to $\text{Co}(\text{OH})_3$, all of which are insoluble in excess of NaOH . Chromium which is present in the solution as sodium chromite NaCrO_2 is oxidized to the more stable sodium chromate Na_2CrO_4 , *e.g.*:



The reason for the oxidation is that more stable, or more insoluble compounds may be formed. In addition, however, if certain combinations of cations are present, complications arise owing to mutual reactions. Zinc and manganese may combine to form insoluble ZnMnO_2 and zinc and chromium to form insoluble ZnCrO_2 thus bring zinc and chromium into the Iron

subgroup. The oxidation of manganese to +4 valence and chromium to +6 obviates this and also makes the identification of chromium somewhat simpler.

It is frequently found that during the course of an analysis time may be saved by observing the colors of solution or precipitate due to the addition of the various reagents. Thus a green solution may indicate the presence of either Ni^{++} or Cr^{+++} or both, but if the addition of NH_4OH produces a blue solution with no precipitate, nickel is present and chromium is absent.

It is important therefore that the appearance of solutions and precipitates obtained during the preliminary experiments be carefully noted.

EXPERIMENTAL

The Aluminum Subgroup

A. PRELIMINARY EXPERIMENTS

1. Aluminum, Al^{+++} . 1. *Hydrolysis of Aluminum Salts.*—Dilute 5 ml. $\text{Al}_2(\text{SO}_4)_3$ solution to 15 ml., divide into three parts, and treat the separate portions as follows, saving precipitates for comparison:

a. Add 5 ml. dilute NH_4OH .

b. Add 5 ml. $(\text{NH}_4)_2\text{S}$ solution (saturate 5 ml. dilute NH_4OH with H_2S).

c. Add 5 ml. $(\text{NH}_4)_2\text{CO}_3$ solution.

Compare the precipitates and write equations for the reactions which have taken place.

2. *Amphoteric Behavior of Aluminum Hydroxide.*—Dilute 2 ml. $\text{Al}_2(\text{SO}_4)_3$ solution to 10 ml. and add 5 ml. dilute NH_4OH . Divide the precipitate into two parts. To one portion add 5 ml. dilute NaOH . Result?

To the other portion add dilute HCl until no further reaction appears to take place. Result?

Write ionic equations for both processes.

3. *Formation of Lakes and Dyes.*—Dilute 2 ml. $\text{Al}_2(\text{SO}_4)_3$ to 10 ml. and add 1 to 2 drops of alizarin reagent. Make the solution slightly alkaline with dilute NH_4OH and heat to boiling. Note the color of the precipitate.

2. Chromium, Cr^{+++} , CrO_4^- , and Cr_2O_7^- .—Note that chromium in the valence state of +3 forms an amphoteric oxide and hydroxide. In the valence state of +6, however, the oxide is entirely acidic.

In the substance to be analyzed, the element may occur either as the chromic salt, e.g., CrCl_3 , or as a chromate or dichromate, e.g., Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$. The latter compounds are readily reduced so that after H_2S has been passed into the solution for the precipitation of Group II the chromium will all be found in the valence of +3.

1. *Hydrolysis of Chromic Salts.*—Dilute 5 ml. CrCl_3 solution to 15 ml., divide into 3 parts, and treat the separate portions as in the case of Aluminum 1. Record the results. Compare the precipitates and write equations for the reactions which have taken place.

2. *Amphoteric Behavior of Chromic Hydroxide.*—Treat 2 ml. CrCl_3 solution according to 2 under Aluminum. Record the results and write the ionic equations.

3. *Oxidation of Cr^{+++} to CrO_4^- .*—Dilute 5 ml. CrCl_3 to 10 ml. in a small beaker. Add slowly 10 ml. of NaOH , noting results. Obtain about 1 g. of solid sodium peroxide from the storeroom. (Note.—Great care must be exercised in handling Na_2O_2 . Transfer it only on dry glass or porcelain—never on paper or on the hands. Any unused portion must be dissolved in water and flushed down the sink. Never throw it into a waste-jar.) Set the beaker in a dish of cold water and add the Na_2O_2 carefully in small portions, stirring with a glass rod. Note the result.

Boil the solution very gently in order to decompose any excess of Na_2O_2 , and then carefully acidify the solution with dilute HNO_3 . Note the result and write the equation.

4. *Reduction of Chromates and Dichromates to Chromic Salts.*—Take two portions of 2 ml. each of $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Add to 1 portion 5 ml. dilute HCl and to the other 5 ml. dilute H_2SO_4 .

Dilute each to 15 ml. and saturate with H_2S . Note any color change and the formation of any precipitate. Write one ionic equation for both reactions.

To 2 ml. of K_2CrO_4 solution add 5 ml. dilute HCl and dilute to 15 ml. Saturate with H_2S as before. Compare the products with those obtained in the previous experiment.

5. *Precipitation of Chromates.*—Dilute three 2 ml. portions of K_2CrO_4 to 10 ml. and treat as follows:

- to one add 2 ml. $\text{Pb}(\text{NO}_3)_2$ solution,
- to another add 2 ml. BaCl_2 solution, and
- to the third add 2 ml. $\text{Sr}(\text{NO}_3)_2$ solution.

Note the results.

Add to each mixture 4 ml. concentrated HCl , shake well, and note any changes. Which of the precipitates are soluble in HCl ?

3. **Zinc Zn^{++} .** 1. *The Zinc Ammonia Complex Ion.*—Dilute 2 ml. $\text{Zn}(\text{NO}_3)_2$ solution to 10 ml. and add dilute NH_4OH drop by drop, noting the result. Now add an excess of NH_4OH . What happens? Write the equation.

Compare this behavior with that obtained with the solutions of Al^{+++} and Cr^{+++} .

2. *Amphoteric Behavior of Zinc Hydroxide.*—Treat 2 ml. $\text{Zn}(\text{NO}_3)_2$ solution according to (2) under Aluminum. Record the results and write the ionic equations.

3. *Precipitation of Zinc Sulfide, ZnS .*—Dilute 2 ml. $\text{Zn}(\text{NO}_3)_2$ solution to 10 ml., add 5 ml. dilute NH_4OH , and saturate with H_2S gas. Shake the mixture well and divide it into three portions:

- to one add 10 drops of dilute HCl ,
- to another add drops of dilute acetic acid, and

to the third add 5 ml. of sodium acetate solution, then 5 drops of dilute HCl . Explain the results in light of the ionic theory.

4. *Precipitation of Zinc Ferrocyanide, $\text{Zn}_2\text{Fe}(\text{CN})_6$.*—Dilute 2 ml. $\text{Zn}(\text{NO}_3)_2$ solution to 10 ml. and add 2 ml. $\text{K}_4\text{Fe}(\text{CN})_6$ solution. Note the result and write the equation.

B. ANALYSIS

We shall first deal with the analysis of a solution containing only the metal ions of the Aluminum subgroup of Group III. It will not be necessary in this case to test for the presence of Group I and Group II metals and since Groups IV and V are likewise absent, the precipitation of Group III metals with $(\text{NH}_4)_2\text{S}$ may be dispensed with.

Procedure. P. 9. *Treatment with NaOH and Na_2O_2 .*—Place 10 ml. of your unknown solution in a small beaker which is set in a dish of water and add NaOH drop by drop until a precipitate appears, then add 5 ml. more. Obtain $\frac{1}{2}$ g. Na_2O_2 from the store room and add this in small portions with continuous stirring. Decompose the excess of Na_2O_2 by boiling the solution for a few minutes.

P. 10. *Aluminum. a. Precipitation.*—To the solution from P. 9 add dilute HNO_3 carefully until the solution is just acid to litmus. Add slowly dilute NH_4OH until the resulting mixture smells strongly of ammonia. Heat to boiling. A gelatinous precipitate indicates the presence of aluminum.

b. *Confirmatory Test.*—Filter the solution and treat the filtrate according to P. 11.

Pour 5 ml. of hot dilute HCl over the precipitate on the filter paper and collect the filtrate in a test tube. Add 3 drops of alizarin reagent and then 10 ml. of filtered NH_4OH (dilute). The formation of a precipitate which absorbs the color of the dye confirms the presence of aluminum.

P. 11. *Chromium. a. Detection.*—Neutralize the filtrate from P. 10 with dilute acetic acid. If the color of the solution is yellow-orange, the presence of chromium as Cr_2O_7 is suggested.

b. *Confirmatory Test.*—By artificial light the solution may appear to be nearly colorless so the confirmatory test should usually be applied. To one-quarter of the solution from (a) add 2 ml. lead nitrate solution. A yellow precipitate of PbCrO_4 indicates chromium.

P. 12. *Zinc.* a. *Precipitation as Sulfide.*—Dilute the remainder of the solution from P. 11a to 50 ml. and saturate with H_2S gas. A white precipitate indicates the possible presence of zinc.

b. *Confirmatory Test.*—If a white precipitate is obtained it may possibly be only free sulfur from the oxidation of the sulfide by the chromate. Filter, rejecting the filtrate. Transfer the precipitate with the filter paper to a small beaker, add a few ml. of nitric acid, and warm. Dilute to 20 ml. filter, rejecting the residue, and neutralize the filtrate carefully with ammonium hydroxide. Add 1 or 2 drops of acetic acid and 3 drops of $\text{K}_4\text{Fe}(\text{CN})_6$ solution. A white precipitate indicates the presence of *zinc*.

TREATMENT OF DATA

1. Write down the results of the preliminary experiments in order, using the numbers of the sections.
2. Make a tabular outline of your analysis, summarize, and write equations for all reactions which have taken place.

EXERCISES

1. Complete the following tabular outline of the analysis of the Aluminum subgroup.

Original Solution		Solution		Ppt.
Al^{+++}	} NaOH	NaAlO_2	} HNO_3	$\text{Al}(\text{OH})_3$
Cr^{+++}		Na_2CrO_4		
Zn^{++}	} Na_2O_2	Na_2ZnO_2	} NH_4OH	
			Soln. } —————> etc.
			 }

2. Why does zinc sulfide not hydrolyze as do the sulfides of aluminum and chromium?
3. An unknown solution is tested for Group II. On passing in H_2S the yellow color of the solution changes to dark green and a white precipitate appears which however does not test for any Group II cation. What element is present?
4. From the fact that zinc forms an ammonia complex ion, devise an alternative scheme of separation and identification of zinc, chromium and aluminum.

ASSIGNMENT 26

GROUP III. THE IRON-ALUMINUM GROUP. THE IRON SUBGROUP

Note.—Students should reread the introductory section of Assignment 25.

EXPERIMENTAL

A. PRELIMINARY EXPERIMENTS

1. Manganese, Mn^{++} and MnO_4^{-} . 1. *Precipitation of Manganous Hydroxide, $Mn(OH)_2$.*—Dilute 2 ml. of manganous nitrate solution to 10 ml. and heat to boiling. This expels dissolved air which would cause oxidation of the precipitate. Add 2 ml. dilute NH_4OH . What happens?

Boil 10 ml. of ammonium nitrate solution and add it to the mixture obtained above. What happens? Save the solution for (2).

Express both the above reactions by a single reversible equation.

2. *Oxidation of $Mn(OH)_2$ to $MnO(OH)_2$.*—Divide the solution from (1) into two parts. To one add carefully $\frac{1}{2}$ g. Na_2O_2 . Note the result. Shake the other portion vigorously with a little water and note any color change.

3. *Precipitation of Manganous Sulfide, MnS .*—Dilute 2 ml. $Mn(NO_3)_2$ solution to 10 ml. Boil, then saturate with H_2S . Note any result. Add 5 ml. of dilute NH_4OH to the solution. What is the precipitate?

4. *Oxidation of Mn^{++} to MnO_2 .*—To 2 ml. $Mn(NO_3)_2$ solution add 10 ml. concentrated HNO_3 and heat to boiling. Add carefully about 1 g. solid $KClO_3$ and boil 2 or 3 min. Note the result.

5. *Oxidation of MnO_2 to MnO_4^{-} .*—Place about $\frac{1}{2}$ g. solid manganese dioxide in a test tube and add $\frac{1}{2}$ g. of solid lead dioxide PbO_2 . Add 10 ml. dilute HNO_3 and boil the liquid. Allow the solid residue to settle and note the color of the solution. Write the equation.

2. Iron Fe^{++} and Fe^{+++} . 1. *Reduction of Ferric Salts.*—Dilute 2 ml. $FeCl_3$ solution to 10 ml. and add 4 ml. dilute HCl . Saturate with H_2S gas and heat to boiling. Note any precipitate and color change. Write the equation. Make the mixture alkaline with NH_4OH . What happens?

2. *Oxidation of Ferrous Hydroxide.*—Dilute 5 ml. ferrous sulphate solution to 15 ml. and add carefully 10 ml. of $NaOH$ solution. Now add $\frac{1}{2}$ g. solid Na_2O_2 to the above mixture and note any color change. Is ferrous hydroxide readily oxidized by the oxygen in the air?

3. *Precipitation of Ferric Hydroxide.*—Dilute 2 ml. $FeCl_3$ solution to 10 ml. and add 5 ml. dilute NH_4OH . Note the result. Does iron form a soluble ammonia complex?

4. *Tests for the Ferric Ion.*—Dilute 2 ml. $FeCl_3$ solution to 10 ml. and divide into two parts. To one add a few drops of ammonium thiocyanate (NH_4CNS) solution. Note the result. To the other add a few drops of potassium ferrocyanide ($K_4Fe(CN)_6$) solution. Note the result.

3. Nickel, Ni^{++} . 1. *Precipitation of Nickel Sulfide, NiS .*—Dilute 2 ml. nickel nitrate $Ni(NO_3)_2$ solution to 10 ml., add 4 ml. dilute HCl and saturate with H_2S . Note the result. Now make the solution alkaline with dilute NH_4OH . Note the result.

2. *The Nickel-ammonia Complex Ion, $Ni(NH_3)_4^{++}$.*—Dilute 2 ml. $Ni(NO_3)_2$ solution to 10 ml. and add an excess of dilute NH_4OH slowly noting the changes taking place. Write the equation. Now pass in H_2S . What happens? Write the ionic equations.

3. *Precipitation of Nickel Hydroxide, $Ni(OH)_2$.*—Dilute 2 ml. $Ni(NO_3)_2$ solution to 10 ml. and add 5 ml. $NaOH$. Add $\frac{1}{2}$ g. solid Na_2O_2 to the mixture and note any change.

4. *Reaction of Ni^{++} with Dimethyl Glyoxime.*—Dilute 2 ml. $\text{Ni}(\text{NO}_3)_2$ solution to 10 ml. and add 2 ml. sodium acetate, then a few drops of dimethyl glyoxime reagent. Note the result.

4. *Cobalt, Co^{++} .* 1. *Precipitation of Cobalt Sulfide, CoS .*—Dilute 2 ml. cobalt nitrate solution to 10 ml., add 4 ml. dilute HCl , and saturate with H_2S . Is there a precipitate? Now make the solution alkaline with dilute NH_4OH . What is formed?

2. *The Cobalt-ammonia Complex Ion, $\text{Co}(\text{NH}_3)_4^{++}$.*—Treat 2 ml. $\text{Co}(\text{NO}_3)_2$ solution as under (2) for nickel and note the results.

3. *Precipitation of Cobalt Hydroxide, $\text{Co}(\text{OH})_2$.*—Treat 2 ml. $\text{Co}(\text{NO}_3)_2$ solution as under (3) for nickel. Is cobalt hydroxide amphoteric?

4. *Reaction of Co^{++} with Dimethyl Glyoxime.*—Treat 2 ml. $\text{Co}(\text{NO}_3)_2$ solution as under (4) for nickel. Note the color change.

5. *Reaction of Co^{++} with Nitrosobeta-naphthol.*—Dilute 2 ml. $\text{Co}(\text{NO}_3)_2$ solution to 10 ml., add 2 ml. sodium acetate solution, and a few drops of nitrosobeta-naphthol solution. What happens?

B. ANALYSIS OF THE IRON SUBGROUP

We shall now carry through the analysis of a solution containing only the ions of the Iron subgroup. In this case it will not be necessary to precipitate with $(\text{NH}_4)_2\text{S}$, nor to make the separation into subgroups with NaOH and Na_2O_2 .

Procedure. P. 13. *Manganese. a. Precipitation.*—To 10 ml. of unknown solution add 15 ml. of concentrated nitric acid and heat to boiling. Add 1 g. of KClO_3 a little at a time and boil for 2 or 3 min. A dark brown precipitate of MnO_2 indicates manganese. Filter, using an asbestos filter, and treat the filtrate by P. 14.

b. *Confirmatory Test.*—Scrape the precipitate from the surface of the asbestos filter with a spatula and transfer it to a small beaker. Add 2 g. of solid PbO_2 and 10 ml. dilute HNO_3 . Boil for about 2 min. A purple solution indicates the presence of *manganese*.

P. 14. *Iron. a. Precipitation.*—Neutralize the filtrate from P. 14 with dilute NH_4OH and add 5 ml. in excess. A reddish-brown gelatinous precipitate indicates the presence of *iron*. Filter and treat the filtrate by P. 15.

b. *Confirmatory Test.*—Dissolve the precipitate in 5 ml. dilute HCl and add to the solution a few drops of NH_4CNS solution. A blood red solution indicates the presence of *iron*.

P. 15. *Nickel.*—Acidify the filtrate from P. 14 with dilute acetic acid. Divide the solution into 2 parts and reserve 1 for P. 16.

To the other add a few drops of dimethyl glyoxime reagent. A pink precipitate indicates the presence of *nickel*. A brown solution indicates the presence of *cobalt*.

P. 16. *Cobalt.*—To the portion of solution reserved from P. 15 add a few drops of nitrosobeta-naphthol reagent. A red precipitate indicates the presence of *cobalt*.

TREATMENT OF DATA

1. Write down the results of the preliminary experiments in order, using the numbers of the sections.

2. Make a tabular outline of your analysis, summarize, and write equations for all reactions which have taken place.

EXERCISES

1. Why do not nickel and cobalt precipitate as hydroxides when the solution is tested for iron with NH_4OH ?

2. Describe an alternative confirmatory test for iron.

3. If manganese was present in solution as potassium permanganate, what effect would be observed in the precipitation of Group II metals?

ASSIGNMENT 27

GROUP III. THE IRON-ALUMINUM GROUP. SEPARATION OF THE IRON AND ALUMINUM SUBGROUPS

EXPERIMENTAL

A. PRELIMINARY EXPERIMENTS

Dilute 2 ml. of ferrous sulfate solution to 10 ml. in a small beaker. Add 2 ml. of chromic chloride solution and make alkaline with dilute NaOH. Note the appearance of the precipitate.

Now add solid Na_2O_2 carefully, with stirring, until there is no further change in color (about 1 g.). Add 10 ml. of water and bring the mixture to the boiling point. Filter while still hot, washing the precipitate carefully with warm water.

Test the filtrate for the presence of Fe^{+++} .

Transfer the precipitate to a small beaker, dissolve in a little dilute HNO_3 by warming, neutralize with dilute NaOH, and then acidify with dilute acetic acid. Test the resulting solution for chromium. From the results you obtain, do you consider the above separation a complete one?

B. ANALYSIS OF ALUMINUM AND IRON SUBGROUPS

The solution to be analyzed here may contain ions of any of the metals of Group III and hence the separation into subgroups must be made. To illustrate the procedure as it would be carried out in practice (where other groups might be present), the precipitation of the group as a whole with $(\text{NH}_4)_2\text{S}$ is also included.

Procedure. P. 17. *Group Precipitation.*—To 15 ml. of the unknown solution add 10 ml. ammonium nitrate solution and heat to boiling. Add slowly 5 ml. dilute NH_4OH , note any changes, and interpret in the light of the preliminary experiments. Without filtering, saturate the solution with H_2S and filter. Test for completeness of precipitation by adding a little NH_4OH to the filtrate and again saturating with H_2S . If further precipitation occurs, filter through the same filter paper. Reject the filtrate, and treat the precipitate by P. 18.

P. 18. *Separation of the Aluminum and Iron Subgroups.*—Transfer the precipitates to a small beaker and add 10 ml. of water and 10 ml. dilute HCl. If a black residue still remains (suggesting the presence of Nickel or Cobalt), add a few drops of concentrated HNO_3 and heat to boiling if necessary repeating the addition of HCl and HNO_3 until any residue is light colored (sulphur).

Filter off and reject the residue. Remove excess acid from the filtrate by evaporating in a small beaker to about 10 ml. Dilute to 15 ml. and add slowly dilute NaOH until reaction appears complete. Set the beaker in a dish of cold water and add slowly with stirring 1 to 2 g. Na_2O_2 .

Boil the mixture for a few minutes to decompose the excess of Na_2O_2 , dilute with an equal volume of water, and filter. The precipitate indicates the presence of the iron subgroup.

Treat the filtrate by P. 10 and subsequent procedures under analysis of the Aluminum subgroup.

Transfer the precipitate to an evaporating dish and add 15 ml. of concentrated HNO_3 . Heat to boiling and add KClO_3 as in P. 13 under analysis of the iron subgroup. Follow the subsequent procedures to the end of the analysis.

TREATMENT OF DATA

Make a tabular outline of your analysis, summarize, and write equations for all reactions which have taken place.

EXERCISES

1. Complete the following tabular outline of Group III analysis:

		<i>Ppt.</i>		
<i>Solution:</i> Cations of Group III	$\left\{ \begin{array}{c} \text{NH}_4\text{OH} \\ \text{H}_2\text{S} \end{array} \right.$		Sulfides and hydroxides of Group III cations	$\left\{ \begin{array}{c} \text{dissolve in HCl.} \\ \text{Add NaOH and Na}_2\text{O}_2 \end{array} \right.$
<i>Ppt.</i>				
Iron subgroup			→ etc.	
<i>Solution</i>				
Aluminum subgroup			→ etc.	

2. If upon addition of NH_4OH to a Group III "unknown" there is no immediate precipitation but on standing a brown precipitate slowly forms, what metal would you suspect as being present?

3. After the addition of NaOH and Na_2O_2 to a certain "unknown" solution the precipitate is black and the solution is colorless. What metals may be present and which is definitely absent?

PROBLEMS

1. A sample of brass weighing 2.6235 g. was dissolved in nitric acid and the lead in the brass was precipitated as PbSO_4 . The precipitate of lead sulfate obtained weighed 0.0147 g. Calculate the percentage of lead in this sample of brass. Ans. 0.383 per cent.

2. In a laboratory experiment a student obtained the following data:

5.60 g. of Ag when converted to AgCl yielded 7.45 g. of AgCl.
3.91 g. of Ag when converted to AgCl yielded 5.20 g. of AgCl.

Show how these results illustrate the law of definite proportions.

3. Three oxyacids of chlorine have the following composition:

H = 1.920 per cent Cl = 67.584 per cent O = 30.514 per cent
H = 1.192 per cent Cl = 41.984 per cent O = 56.824 per cent
H = 1.003 per cent Cl = 35.294 per cent O = 63.703 per cent

Show that these values illustrate the law of multiple proportions.

4. A sample of pure iron wire weighing 1.150 g. was dissolved in nitric acid, the solution evaporated to dryness, and the iron nitrate decomposed to iron oxide by heating. The weight of iron oxide obtained was 1.644 g.

a. If 1.150 is taken as the combining weight of iron, find a combining weight for oxygen.

b. Calculate two other combining weights for iron using as a standard $\text{O} = 16$ and $\text{O} = 8$, respectively.

What do we call values obtained on the latter basis?

Find the ratio of this last combining weight of iron to its atomic weight. Ans. (a) 0.494; (b) 37.25, 18.62.

5. Calculate the percentage composition of $\text{K}_2\text{Cr}_2\text{O}_7$.

Ans. K, 26.58 per cent; Cr, 35.35 per cent; O, 38.07 per cent.

6. Derive the empirical formula of the substance which analyzes 32.54 per cent K, 26.68 per cent S, 39.94 per cent O, and 0.84 per cent H.

7. Calculate the weight of sodium chloride necessary to produce 10 tons of concentrated hydrochloric acid, which contains 40 per cent by weight of HCl. Ans. 6.4 tons.

8. If a quantity of moist nitrogen has a volume of 25 ml. when the barometric pressure is 750 mm. and the temperature 16°C ., what would be the volume when dry at 20°C . and 760 mm.? Ans. 24.56 c.c.

9. When 2.71 g. of a metal are acted upon by hydrochloric acid, they liberate 3.77 l. of H_2 measured over water at 763.7 mm. and 25°C . What is the equivalent weight of the metal? Ans. 9.02.

10. At 177°C . and 760 mm., 225 ml. of acetic acid vapor weighed 0.37 g. Find the molecular weight of acetic acid. Ans. 60.7.

11. An automobile radiator contained 15 l. of water and 4 kg. of anti-freeze, methyl alcohol, CH_3OH . What will be the freezing point of this solution in degrees Centigrade? In degrees Fahrenheit? Ans. -15.5°C ., $+4.1^\circ\text{F}$.

12. When 2.23 g. of cane sugar were dissolved in 100 g. of water, the freezing point of the water was depressed 0.121°C . Calculate the molecular weight of sugar. Ans. 342.5.

13. A solution of 3.04 g. of benzoic acid in 100 g. of alcohol boils 0.288°C . higher than pure alcohol. Find the molecular weight of benzoic acid. Molecular elevation for alcohol = 1.15°C . Ans. 121.3.

14. It is desired to find the atomic weight of an element R . Four volatile compounds of this element are analyzed and their molecular weights obtained by the vapor-density method. The elementary substance R is also volatile at high temperatures so that its molecular weight may be obtained.

The following data are obtained:

a. At 645°C . and 760 mm. pressure, 250 ml. of the simple substance R weighed 1.0 g.

b. At 21°C . and 760 mm., 600 ml. of the hydride weighed 1.95 g. This compound contains 96.12 per cent R .

c. At 174°C . and 765 mm., 400 ml. of the chloride weighed 2.0 g. It contained 58.67 per cent Cl.

d. At 527°C . and 720 mm., 209 ml. of the oxide weighed 0.6 g. It contained 24.26 per cent O.

e. At 273°C . and 760 mm., 500 ml. of another compound of R weighed 1.7 g. It contained 49.30 per cent R .

Calculate first the approximate atomic weight of R as given by these data. Then determine the equivalent weight, the valence, and the exact atomic weight of the element R .

Write the formulas for the hydride, chloride, and oxide of R .

Ans. 75.4, 24.975, 3, 74.93.

15. The specific heat of an element is 0.048 cal. per degree Centigrade. What can you say of its atomic weight? The chloride of this element contains 21.08 per cent chlorine. What is the exact atomic weight of the other element? What is its valence? *Ans.* 132.8, 1.

16. A compound contains 28.22 per cent potassium, 46.19 per cent oxygen, and another element *R*. It is isomorphous with potassium permanganate, KMnO_4 . Find the atomic weight of *R*. *Ans.* 35.46.

17. The laboratory dilute sulfuric acid has a specific gravity of 1.18 and contains 24.6 per cent H_2SO_4 by weight.

a. Find the concentration of H_2SO_4 : (1) in grams per 100 ml. of water; (2) in moles per liter of solution.

b. Calculate the normality of the solution. *Ans.* (a, 1) 32.7 g. per 100 ml., (a, 2) 2.96 moles; (b) 5.92 *N*.

18. For metathetical reactions, how many grams of each of the following should be used for a liter of normal solution? NaOH , H_2SO_4 , H_3PO_4 , $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

State in each case the ratio of the equivalent weight to the molecular weight.

Ans. 40.01, 49.04, 32.68, 122.16.

19. The solubility of lead chromate at 18°C . is 2×10^{-6} g. per 100 ml. of water. Express this in terms of moles per liter of solution.

Ans. 6.19×10^{-7} *M*.

20. An acid solution is standardized by titrating pure sodium carbonate, using methyl orange as an indicator. Of the acid solution 45.1 ml. are required to react with 2.406 g. of sodium carbonate. Find the normality of the acid. *Ans.* 1.006 *N*.

21. Of a nitric acid solution 50 ml. are added to 0.453 g. of calcium carbonate. The excess of acid is titrated by a solution of a base, and 6.15 ml. of the latter are required. The base is then titrated against the acid, and 21.3 ml. of acid require 19.2 ml. of base. Find the normality of the acid and base. *Ans.* 0.210 *N*, 0.233 *N*.

22. What weight of BaCl_2 is needed to precipitate completely, BaSO_4 from 30.5 ml. of 0.1 *N* H_2SO_4 ?

Ans. 0.3176 g.

23. A sample of fertilizer weighing 0.5 g. is heated with concentrated H_2SO_4 until the contained nitrogen is converted into $(\text{NH}_4)_2\text{SO}_4$. The mixture is now neutralized with NaOH and the liberated NH_3 passed into 30 ml. of 0.1875 *N* H_2SO_4 . This neutralizes a part of the acid and the excess is titrated with 0.196 *N* NaOH , requiring 22.05 ml. of base. Calculate (a) the volume of H_2SO_4 neutralized by the NH_3 , (b) the weight of NH_3 present, (c) the percentage of nitrogen in the fertilizer. *Ans.* (a) 6.95 ml.; (b) 0.0222 g.; (c) 3.65 per cent.

24. Formulate the mass-law expression for the reversible reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$. At 630°C . and 760 mm. pressure, an equilibrium mixture is found to contain,

$\frac{1}{3}$ mole of SO_2 , $\frac{1}{6}$ mole of O_2 , and $\frac{2}{3}$ mole of SO_3 .

Calculate (a) The volume occupied by the mixture at the given temperature and pressure; (b) the concentrations in moles per liter of the three constituents; (c) The equilibrium constant of the reaction. *Ans.* (a) 86.51; (b) ?; (c) 2075.

25. A current of 0.4 amp. is passed for 1 hr. and 30 min. through aqueous solutions of sulfuric acid, silver nitrate, cupric sulfate, and cadmium sulfate, arranged in series. What is the weight of each substance evolved or deposited at the electrodes in the series? *Ans.* O_2 0.717 g., Ag 2.42 g., H_2 0.023 g., Cu 0.714 g., Cd 1.26 g.

26. Ten grams of sodium sulfate, Na_2SO_4 , are dissolved in 600 g. of water. The boiling point of the solution at 760 mm. is 100.15°C . What is the apparent degree of ionization? *Ans.* 0.74.

27. Calculate the concentration of H_3O^+ and OH^- in (a) 0.1 *N* NaCl , (b) 0.1 *N* HCl , (c) 0.1 *N* NaOH , (d) $\text{Ca}(\text{OH})_2$ solution containing 1.48 g. of $\text{Ca}(\text{OH})_2$ per liter. Assume all of these substances to be completely ionized. Calculate the pH of each solution.

Ans. (a) $[\text{H}_3\text{O}^+] 10^{-7}$ *M*, $[\text{OH}^-] 10^{-7}$ *M*; (b) $[\text{H}_3\text{O}^+] 10^{-1}$ *M*, $[\text{OH}^-] 10^{-13}$ *M*; (c) $[\text{H}_3\text{O}^+] 10^{-13}$ *M*, $[\text{OH}^-] 10^{-1}$ *M*; (d) $[\text{H}_3\text{O}^+] 2.5 \times 10^{-13}$ *M*, $[\text{OH}^-] 4 \times 10^{-2}$ *M*.

28. The equivalent conductivity of 0.1 *M* NH_4OH is 3.24 mhos at 18°C . The equivalent conductivity at infinite dilution is 238.4 mhos.

a. Calculate the degree of ionization in such a solution.

b. What is the ionization constant at 18°C .?

c. Calculate the degree of ionization and the concentration of OH^- (1) in 0.01 *M* NH_4OH , (2) in 1.00 *M* NH_4OH .

Ans. (a) 1.36×10^{-2} ; (b) 1.87×10^{-5} ; (c, 1) $\alpha = 4.23 \times 10^{-2}$, $[\text{OH}^-] = 4.23 \times 10^{-4}$, (2) $\alpha = 4.33 \times 10^{-3}$, $[\text{OH}^-] = 4.33 \times 10^{-3}$.

29. The ionization constant of HNO_2 (nitrous acid) is 4.5×10^{-4} at 25°C . Calculate its degree of ionization; (a) in a solution 0.1 *M* in HNO_2 , (b) in a solution 0.1 *M* in HNO_2 and 0.1 *M* in NaNO_2 , (c) in a solution 0.1 *M* in HNO_2 and 0.1 *M* in HNO_3 . *Ans.* (a) 0.065; (b) 0.0045; (c) 0.0045.

30. A solution contains 8 ml. of 6 *N* $\text{HC}_2\text{H}_3\text{O}_2$ in 400 ml. of solution. To this is added 7.7 g. of ammonium acetate. The ionization constant of acetic acid is 1.86×10^{-5} at 25°C . Calculate the $[\text{H}_3\text{O}^+]$ in this solution.

Ans. 8.92×10^{-6} *M*.

31. A solution is known to contain 3 ml. of 5 *N* NH_4OH in 75 ml. of solution. In this solution the NH_4OH is ionized 0.95 per cent. To the solution is added 0.125 mole of ammonium chloride. Calculate the hydroxyl ion concentration in this solution. *Ans.* 2.19×10^{-5} *M*.

32. Sulfuric acid in 0.05 *M* solution is completely ionized into H_3O^+ and HSO_4^- . The ionization constant for the secondary ionization is 2.0×10^{-2} at 18°C.

a. What is the concentration in the solution of each of the following? (1) H_3O^+ , (2) HSO_4^- , (3) SO_4^{2-} ,

b. What is the freezing point of this solution? *Ans.* (a, 1) 0.0622, (2) 0.0378, (3) 0.0122; (b) -0.209°C .

33. The ionization constant of NH_4OH is 1.8×10^{-5} at 25°C. Calculate the degree of hydrolysis and the H_3O^+ concentration in 0.1 *M* NH_4Cl solution. *Ans.* 7.46×10^{-5} , $[\text{H}_3\text{O}^+] = 7.46 \times 10^{-6}$ *M*.

34. The ionization constant of HCN is 7.2×10^{-10} at 25°C. Using the data of the previous problem, calculate the hydrolysis constant for NH_4CN . Calculate the degree of hydrolysis of 0.1 *M* NH_4CN . *Ans.* $K_H = 0.772$, 46.8 per cent.

35. The solubility product of strontium chromate is 3.6×10^{-5} at 25°C. Would a precipitate form if equal portions of 0.002 *M* $\text{Sr}(\text{NO}_3)_2$ and 0.002 *M* K_2CrO_4 were mixed?

36. The solubility of KClO_4 in water at 25°C. is 0.148 mole per liter. Calculate its solubility in a solution containing 0.1 mole per liter of KCl . *Ans.* 0.106 *M*.

37. a. A liter of water dissolves 0.025 mole of AgBrO_3 at 18°C. What is the solubility product of AgBrO_3 ?

b. When 1 ml. of 1.0 *M* NaBrO_3 is added to 10 ml. of 0.05 *M* AgNO_3 will precipitation occur?

Ans. (a) 0.000625. *

38. a. The solubility product of copper sulfide is 8.5×10^{-46} at 18°C. That of zinc sulfide is 1.2×10^{-23} . A solution 0.1 *M* in copper nitrate, 0.1 *M* in zinc nitrate, and 0.3 *M* in HNO_3 is saturated with H_2S (solubility 0.1 mole per liter). The ionization constants of H_2S are, $k_1 = 9.0 \times 10^{-8}$, $k_2 = 1 \times 10^{-15}$.

Calculate the concentrations of Cu^{++} and Zn^{++} left in solution.

Ans. $[\text{Cu}^{++}] = 8.5 \times 10^{-23}$ *M*, $[\text{Zn}^{++}] = 0.1$ *M*.

How much of the copper has been precipitated as sulfide? Of the zinc?

b. The mixture from the above treatment is filtered and the filtrate neutralized with NH_4OH , and again saturated with H_2S . What is the concentration of Zn^{++} now left in solution? *Ans.* 1.2×10^{-8} *M*.

How much zinc has precipitated as sulfide?

APPENDIX

I. CONCENTRATIONS OF COMMON REAGENTS

I. Desk reagents.

A. Concentrated acids and bases.

Hydrochloric acid, 12 *N*.

Use c.p. acid 38 per cent HCl, sp. gr. 1.19.

Nitric acid, 16 *N*.

Use c.p. acid 70 per cent HNO₃, sp. gr. 1.42.

Sulfuric acid, 36 *N*.

Use c.p. acid 95 per cent H₂SO₄, sp. gr. 1.84.

Ammonium hydroxide, 15 *N*.

Use c.p. NH₄OH 28 per cent NH₃, sp. gr. 0.90.

B. Dilute acids and bases.

Hydrochloric acid, 6 *N*.

Mix 12 *N* HCl with an equal volume of water.

Nitric acid, 6 *N*.

Mix 380 ml. of 16*N* HNO₃ with 620 ml. of water.

Sulfuric acid, 6 *N*.

Pour 1 volume of 95 per cent H₂SO₄ into 5 volumes of water.

Acetic acid, 6 *N*.

Mix 350 ml. of 99.5 per cent acid with 650 ml. of water.

Sodium hydroxide, 6 *N*.

Add to 250 g. of NaOH enough water to make the volume 1000 ml.

Ammonium hydroxide, 6 *N*.

Mix 400 ml. of 15 *N* NH₄OH with 600 ml. of water.

II. Side-shelf reagents.

Solutions of salts 1 *N* unless otherwise specified.

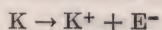
II. VAPOR-PRESSURE OF WATER (Pressure in millimeters of mercury)

Temperature, degrees Centigrade	Millimeters	Temperature, degrees Centigrade	Millimeters
0	4.57	21	18.47
1	4.91	22	19.63
2	5.27	23	20.86
3	5.66	24	22.15
4	6.07	25	23.52
5	6.51	26	24.96
6	6.97	27	26.47
7	7.47	28	28.06
8	7.99	29	29.74
9	8.55	30	31.51
10	9.14	31	33.37
11	9.77	32	35.32
12	10.43	33	37.37
13	11.14	34	39.52
14	11.88	35	41.78
15	12.67	36	44.16
16	13.51	37	46.65
17	14.40	38	49.26
18	15.33	39	52.00
19	16.32	40	54.87
20	17.36		

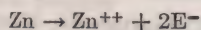
III. ELECTROMOTIVE SERIES

Metals	Non-metals
Lithium	Fluorine
Potassium	Chlorine
Sodium	Bromine
Strontium	Iodine
Barium	Sulfur
Calcium	
Magnesium	
Aluminum	
Manganese	
Zinc	
Chromium	
Iron	
Cadmium	
Cobalt	
Nickel	
Tin	
Lead	
Hydrogen	
Antimony	
Bismuth	
Arsenic	
Copper	
Mercury	
Silver	
Platinum	
Gold	

Note.—This arrangement is based on the tendencies of the elements to take up the ionic state. For example the reaction



has a greater tendency to take place than the reaction



In the case of the non-metals not all of these elements are capable of forming free ions, elements like C, N, and P forming only compound ions like CO_3^{--} , NO_3^- and PO_4^- . Only those non-metals which form free negative ions (F^- , Cl^- , etc.), are included in this table.

IV. OXIDATION-REDUCTION POTENTIALS AT 25°C.

Reaction		Potential, volts
(Reduced form)	(Oxidized form)	
Na	= Na ⁺ + E ⁻	+2.712
Al	= Al ⁺⁺⁺ + 3E ⁻	+1.7
Zn	= Zn ⁺⁺ + 2E ⁻	+0.758
Cr ⁺⁺	= Cr ⁺⁺⁺ + E ⁻	+0.4
H ₂	= 2H ⁺ + 2E ⁻	0.00
Sn ⁺⁺	= Sn ⁺⁺⁺⁺ + 2E ⁻	-0.13
Cu ⁺	= Cu ⁺⁺ + E ⁻	-0.17
H ₂ S	= S + 2H ⁺ + 2E ⁻	-0.17
Cu	= Cu ⁺⁺ + 2E ⁻	-0.344
4OH ⁻	= O ₂ + 2H ₂ O + 4E ⁻	-0.40
2I ⁻	= I ₂ + 2E ⁻	-0.535
H ₂ O ₂	= O ₂ + 2H ⁺ + 2E ⁻	-0.68
Fe ⁺⁺	= Fe ⁺⁺⁺ + E ⁻	-0.74
NO + 2H ₂ O	= NO ₃ ⁻ + 4H ⁺ + 3E ⁻	-0.94
I ⁻ + 3H ₂ O	= IO ₃ ⁻ + 6H ⁺ + 6E ⁻	-1.09
Cr ⁺⁺⁺ + 4H ₂ O	= HCrO ₄ ⁻ + 7H ⁺ + 3E ⁻	-1.3
Mn ⁺⁺ + 2H ₂ O	= MnO ₂ + 4H ⁺ + 2E ⁻	-1.33
2Cl ⁻	= Cl ₂ + 2E ⁻	-1.359
Cl ⁻ + 3H ₂ O	= ClO ₃ ⁻ + 6H ⁺ + 6E ⁻	-1.45
Cl ⁻ + H ₂ O	= HClO + H ⁺ + 2E ⁻	-1.50
Mn ⁺⁺ + 4H ₂ O	= MnO ₄ ⁻ + 8H ⁺ + 5E ⁻	-1.52
O ₂ + H ₂ O	= O ₃ + 2H ⁺ + 2E ⁻	-1.9
2F ⁻	= F ₂ + 2E ⁻	-2.8

Strength of reducing agents

Strength of oxidizing agents

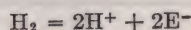
Reducing action

Oxidizing action

E⁻ stands for
one electron

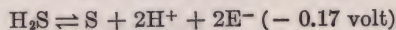
For simplicity, the proton has been written without the accompanying water of hydration. Thus wherever H⁺ appears, H₃O⁺ is to be understood.

Use of the Table.—This table affords a classification of oxidizing and reducing agents. The tendency for a substance to go from the oxidized to the reduced state may be measured electrically by setting up a galvanic cell in which the substance is at one electrode. The potentials shown here have been obtained chiefly in this way and are referred to hydrogen as a standard, the reaction



taking place at the other electrode and being assumed to have zero potential. The potential produced is found to depend on the concentration of the substances involved, so that the values given here all refer to the case where all dissolved substances are 1 molal and all gases are at 1 atmosphere pressure. For this reason these values are sometimes spoken of as "molal oxidation-reduction potentials."

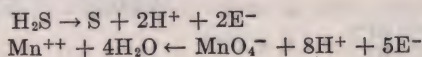
Since loss of electrons indicates oxidation, the substances to the left of the equal sign are being oxidized, and the substances to the right being reduced in the reversible reaction. *In order to make a complete reaction, two of these half reactions must be combined*, and the rule is that any half reaction going from left to right will cause any other half reaction below it on the table to go from right to left; for example, we wish to know whether H₂S will reduce KMnO₄ (in acid solution). The reaction



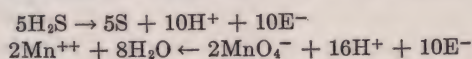
has a higher potential than the reaction



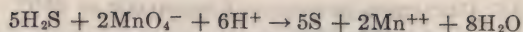
and hence the reactions will go in the directions indicated below:



The electrons given up in one reaction must be used up in the other and hence we have:



Combining and canceling,



which gives a balanced oxidation-reduction equation. Moreover, the potential in volts which this reaction could produce if carried out in a galvanic cell would be $-0.17 \text{ volt} - (-1.52 \text{ volts}) = 1.35 \text{ volts}$, assuming that all substances are present at 1 molal concentration.

We see therefore that the substances on the *left-hand side* of the equal signs are arranged in order of *decreasing activity as reducing agents*, while the substances on the *right-hand side* are arranged in order of *increasing activity as oxidizing agents*.

It is also to be noticed that this table is merely an enlarged form of the electromotive series, and the basis of classification in each table is the same. A few of the metals have been shown on this table to indicate their relations to the other oxidizing and reducing agents.

V. DISSOCIATION CONSTANTS OF WEAK ELECTROLYTES AT 25°C.

Electrolytes	K_1	K_2	K_3
Acids:			
Acetic, $\text{HC}_2\text{H}_3\text{O}_2$	1.86×10^{-5}		
Arsenic, H_3AsO_4	5×10^{-3}	4×10^{-5}	6×10^{-10}
Arsenious, H_3AsO_3	6×10^{-10}		
Boric, H_2BO_3 or HBO_2	6.4×10^{-10}		
Carbonic, H_2CO_3	3.3×10^{-7}	3.9×10^{-11}	
Hydrocyanic, HCN	7.2×10^{-10}		
Hydrofluoric, HF	7.9×10^{-4}		
Hydrosulfuric, H_2S	9.1×10^{-8}	1.2×10^{-15}	
Hypochlorous, HClO	4.4×10^{-8}		
Iodic, HIO_3	1.9×10^{-1}		
Nitrous, HNO_2	4.5×10^{-4}		
Oxalic, $\text{H}_2\text{C}_2\text{O}_4$	3.8×10^{-2}	4.9×10^{-5}	
Periodic, HIO_4	2.3×10^{-2}		
Phosphoric, H_3PO_4	1.1×10^{-2}	2.0×10^{-7}	3.6×10^{-13}
Phosphorous, H_3PO_3	5×10^{-2}	2×10^{-5}	
Pyrophosphoric, $\text{H}_4\text{P}_2\text{O}_7$	1.4×10^{-1}	1.1×10^{-2}	2.9×10^{-7} ($K_4 = 3.6 \times 10^{-9}$)
Selenious, H_2SeO_3	3×10^{-3}	5×10^{-8}	
Sulfuric, H_2SO_4	1.1×10^{-2}	
Sulfurous, H_2SO_3	1.7×10^{-2}	5×10^{-6}	
Telluric, H_2TeO_4	6×10^{-7}	4×10^{-11}	

K

Bases:

Ammonium hydroxide, NH_4OH	1.8×10^{-5}
Silver hydroxide, AgOH	1.1×10^{-4}

Amphoteric hydroxide:

Zinc hydroxide $\left\{ \begin{array}{l} \text{H}_2\text{ZnO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HZnO}_2^- \\ \text{Zn}(\text{OH})_2 \rightleftharpoons \text{Zn}^{++} + 2\text{OH}^- \end{array} \right.$	K 3.5×10^{-25} 1×10^{-9}
--	--

Water:

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

Examples:

$$\frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

$$\frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 1.1 \times 10^{-2} \quad \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^-]}{[\text{H}_2\text{PO}_4^-]} = 2.0 \times 10^{-7}$$

$$\frac{[\text{H}_3\text{O}^+][\text{PO}_4^{=}] }{[\text{HPO}_4^-]} = 3.6 \times 10^{-13}$$

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.8 \times 10^{-5}$$

VI. SOLUBILITY PRODUCTS. ROOM TEMPERATURE

K

Bromides:

$$\text{Silver bromide, } [\text{Ag}^+] \times [\text{Br}^-] = 7.7 \times 10^{-13}$$

Carbonates:

$$\text{Lead carbonate, } [\text{Pb}^{++}] \times [\text{CO}_3^{--}] = 3.3 \times 10^{-14}$$

$$\text{Barium carbonate, } [\text{Ba}^{++}] \times [\text{CO}_3^{--}] = 7 \times 10^{-9}$$

$$\text{Strontium carbonate, } [\text{Sr}^{++}] \times [\text{CO}_3^{--}] = 2 \times 10^{-9}$$

$$\text{Calcium carbonate, } [\text{Ca}^{++}] \times [\text{CO}_3^{--}] = 8.7 \times 10^{-9}$$

$$\text{Magnesium carbonate, } [\text{Mg}^{++}] \times [\text{CO}_3^{--}] = 2.6 \times 10^{-5}$$

Chlorides:

$$\text{Silver chloride, } [\text{Ag}^+] \times [\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$\text{Cuprous chloride, } [\text{Cu}^+] \times [\text{Cl}^-] = 1 \times 10^{-6}$$

$$\text{Lead chloride, } [\text{Pb}^{++}] \times [\text{Cl}^-]^2 = 2.4 \times 10^{-4}$$

$$\text{Mercurous chloride, } [\text{Hg}^+] \times [\text{Cl}^-] = 3 \times 10^{-13}$$

Chromates:

$$\text{Lead chromate, } [\text{Pb}^{++}] \times [\text{CrO}_4^{--}] = 1.8 \times 10^{-14}$$

$$\text{Barium chromate, } [\text{Ba}^{++}] \times [\text{CrO}_4^{--}] = 2.2 \times 10^{-10}$$

$$\text{Strontium chromate, } [\text{Sr}^{++}] \times [\text{CrO}_4^{--}] = 3.6 \times 10^{-5}$$

$$\text{Silver chromate, } [\text{Ag}^+]^2 \times [\text{CrO}_4^{--}] = 3.3 \times 10^{-12}$$

Hydroxides:

$$\text{Aluminum hydroxide, } [\text{Al}^{+++}] \times [\text{OH}^-]^3 = 3.7 \times 10^{-15}$$

$$\text{Chromium hydroxide, } [\text{Cr}^{+++}] \times [\text{OH}^-]^3 = 4 \times 10^{-32}$$

$$\text{Cupric hydroxide, } [\text{Cu}^{++}] \times [\text{OH}^-]^2 = 2 \times 10^{-13}$$

$$\text{Ferric hydroxide, } [\text{Fe}^{+++}] \times [\text{OH}^-]^3 = 1 \times 10^{-36}$$

$$\text{Magnesium hydroxide, } [\text{Mg}^{++}] \times [\text{OH}^-]^2 = 3 \times 10^{-11}$$

$$\text{Manganese hydroxide, } [\text{Mn}^{++}] \times [\text{OH}^-]^2 = 4 \times 10^{-14}$$

Iodides:

$$\text{Lead iodide, } [\text{Pb}^{++}] \times [\text{I}^-]^2 = 2 \times 10^{-8}$$

$$\text{Silver iodide, } [\text{Ag}^+] \times [\text{I}^-] = 1.5 \times 10^{-16}$$

Sulfides:

$$\text{Mercuric sulfide, } [\text{Hg}^{++}] \times [\text{S}^{--}] = 1 \times 10^{-53}$$

$$\text{Silver sulfide, } [\text{Ag}^+]^2 \times [\text{S}^{--}] = 1.6 \times 10^{-49}$$

$$\text{Cuprous sulfide, } [\text{Cu}^+]^2 \times [\text{S}^{--}] = 2 \times 10^{-47}$$

$$\text{Cupric sulfide, } [\text{Cu}^{++}] \times [\text{S}^{--}] = 8.5 \times 10^{-45}$$

$$\text{Cadmium sulfide, } [\text{Cd}^{++}] \times [\text{S}^{--}] = 1 \times 10^{-29}$$

$$\text{Lead sulfide, } [\text{Pb}^{++}] \times [\text{S}^{--}] = 4.2 \times 10^{-28}$$

$$\text{Zinc sulfide, } [\text{Zn}^{++}] \times [\text{S}^{--}] = 1.2 \times 10^{-23}$$

$$\text{Ferrous sulfide, } [\text{Fe}^{++}] \times [\text{S}^{--}] = 1 \times 10^{-19}$$

$$\text{Manganese sulfide, } [\text{Mn}^{++}] \times [\text{S}^{--}] = 1.4 \times 10^{-15}$$

VII. COMPLEX CONSTANTS. TEMPERATURE 25°C.

K

Ion:

$$\text{Ag}(\text{NH}_3)_2^+ \dots\dots\dots 7 \times 10^{-8}$$

$$\text{Ag}(\text{CN})_2^- \dots\dots\dots 1 \times 10^{-21}$$

$$\text{Cd}(\text{CN})_4^{--} \dots\dots\dots 1.8 \times 10^{-13}$$

$$\text{Cu}(\text{CN})_3^- \dots\dots\dots 5 \times 10^{-23}$$

Example:

$$\frac{[\text{Cu}^+][\text{CN}^-]^3}{[\text{Cu}(\text{CN})_3^-]} = 5 \times 10^{-23}$$

VIII. MOLECULAR AND ATOMIC CONSTANTS

$$\text{Gas constant, } R \dots\dots\dots 82.07$$

(Pressure in atmospheres, volume in cubic centimeters)

$$\text{Gram-molecular volume} \dots\dots\dots 22.4 \text{ liters}$$

$$\text{Molal lowering of the freezing point for water} \dots\dots\dots 1.858^\circ$$

$$\text{Molal elevation of the boiling point for water} \dots\dots\dots 0.515^\circ$$

$$\text{Number of molecules in 1 mole} \dots\dots\dots 6.06 \times 10^{23}$$

$$\text{Diameter of the oxygen molecule} \dots\dots\dots 2.9 \times 10^{-8} \text{ cm.}$$

$$\text{Mass of the hydrogen atom} \dots\dots\dots 1.66 \times 10^{-24} \text{ g.}$$

12. RECORD FORM FOR QUALITATIVE ANALYSIS

Name _____

Section _____

Date _____

Report on analysis of _____

Unknown solution No. _____

Substance

Procedure

Result

Interference

A PERIODIC CHART OF THE ATOMS
Showing the Number of Electrons in the various Shells also Atomic Numbers and Atomic Weights

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1st	H	He																
2nd	Li	Be	B	C	N	O	F	Ne										
3rd	Na	Mg	Al	Si	P	S	Cl	Ar										
4th	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5th	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6th	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Rn
7th	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

PERIODIC CHART OF THE ATOMS

Period

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1st	H	He																
2nd	Li	Be	B	C	N	O	F	Ne										
3rd	Na	Mg	Al	Si	P	S	Cl	Ar										
4th	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5th	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6th	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Rn
7th	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Atomic number

Lead nitrate

Potassium dichromate

Barium chloride

Magnesium sulfate

Calcium chloride

Sodium chloride

Ammonium chloride

Carbonic acid

Barium chloride

Potassium dichromate

Barium chloride

Magnesium sulfate

Calcium chloride

Sodium chloride

Ammonium chloride

Carbonic acid

Note: The numbers in the boxes are the atomic numbers of the elements in the periodic system.

The order given is approximately that in which these reagents appear in the experiments. The common acids and bases are omitted.

HIS